開発高性能水系塗料の展開とその流動性の解析

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DEVELOPMENT OF HIGH PERFORMANCE, WATERBORNE COATINGS
AND THE ANALYSIS OF THEIR LEVELING FLOW

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AND THE ANALYSIS OF THEIR LEVELING FLOW

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CHAPTER 1. INTRODUCTION

1-1. General Background

The production of metal cans for food and beverage use in Japan was estimated to exceed 38 billion in 1994. The consumption of coating materials in the can manufacturing industry was estimated to be about 70,000 tons, which is one of the major segments in the coating industry, about one fifth of that for the automobile industry.

Comparative with the US foods and beverage market, however, non-carbonated beverages such as coffee drinks, tea and fruit drinks are the largest segment in Japan, about two thirds of canned foods and beverages. Drawn and wall ironed, DWI, cans are feasible to use for carbonated beverages and beer, and have several economical advantages, such as use of less metal material. However, most of the non-carbonated beverages and foods are filled in rigid three-piece cans, because such products need to be hot-filled and/or retort sterilized and the inside of the cans is kept vacuum in the market place. Although liquid nitrogen injection filling systems and relatively rigid stretch drawn cans from polyester laminated steel have been developed, the majority of non-carbonated beverages and foods are still filled in three-piece cans.

At our company, Toyo Seikan Kaisha, Ltd., the sideseam bonded cans called "Toyo Seam Cans" were developed about 25 years ago and then improved for hot-filled and/or retort sterilized foods and beverages\(^{1,2}\). In 1991, the production of the sideseam bonded cans was estimated to be about one fourth of that
of metal cans for foods and beverage application. The improvements of the sideseam bonded cans to apply for such heat processed foods and beverages include the surface treatment of the steel substrate, the adhesive and the adhesion primer\textsuperscript{[2]}. Figure 1-1 shows the sideseam structure of "Toyo Seam Can".\textsuperscript{[1]}

![Diagram of sideseam bonded portion of Toyo Seam Can]

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Fig_1-1.png}
\caption{Cross-sectional view of bonded portion of Toyo Seam Can}
\end{figure}

All the constituent materials play important roles to promote reliable adhesion; the adhesive, tin free steel, TFS, and the adhesion primer. A thermoplastic polyamide is utilized as the adhesive. The surface treatment of TFS is important to achieve strong adhesion, and specially designed electro-chromium coated steel is utilized. The waterborne adhesion primer is the target of development. A specially designed epoxy/phenolic solvent borne coating, SBC, has been used as an adhesion primer for the cans since the can was first developed.

In the can manufacturing industry, as well as in other industries, the demands toward coatings with higher performance
are very strong. Coatings with higher adhesion performance, better corrosion resistance, higher flexibility, higher sulfide stain resistance and so on, are desired. These trends toward higher performance coatings in container applications have shown a need for properties characteristic of the component resins, epoxy and hardeners, and these resin have been effectively improved\cite{3-5}. These resins show excellent performance when used as a component of SBCs. However, their performances are not satisfactory when used in waterborne coatings, WBCs, made by the conventional processes. On the other hand, as noted below, it has become quite important to develop WBCs with excellent performances including adhesion performance and to apply them for commercial production.

1-2. Waterborne Coatings

In recent years, it is strictly required to reduce the emission of volatile organic compounds, VOC, besides sulfur oxides, \(SO_x\), nitrogen oxides, \(NO_x\), and carbon dioxide, \(CO_2\), from coating facilities to protect the earth. Thus, studies have been concentrated to develop compliant coatings in the coating industry, which include WBCs, higher solids, powder coatings, ultraviolet light curable coatings, electron beam curable coatings, film lamination and so on. Among those compliant coatings, WBCs have been most widely applied in many industries and most of the coatings for DWI cans have been changed to WBCs all over the world.

There are several advantages of using WBCs such as:

1. Reduced volume of organic solvents emitted from the plant,
thus reducing the adverse effects on the environment.

(2) Reduction of the organic solvent level in the working environment, thus improving the standards of occupational health and safety.

(3) Reduced risk of fire.

(4) Reduced usage of organic solvents, thus saving resources.

(5) No necessity to install after-burners to save energy.

For these reasons, great efforts have been made to develop WBCs in a variety of industries. Today waterborne house paints and repair paints are commonly used. In the automobile industry, it has become common to use a waterborne primer applied by electrocoating. These trends were precisely reviewed by Bauer[6] and Emch[7].

Both water soluble resins and water dispersible resins are used for WBCs in the can manufacturing industry. Water soluble resins are mainly used for the exterior coatings while water dispersible resins are used for the interior coatings of DWI cans. Water soluble resins are mainly acrylic resins, polyester and amino resins, the performances of which are limited when used as can coatings, for example, adhesion, corrosion resistance, etc. Thus, water soluble resins have established their position as overprint varnishes and as binders of a white base coat. On the other hand, water dispersible resins, which are mainly modified epoxy resins, are used as interior coatings of food and beverage cans[8-11]. The performances of this type of coatings are excellent for these applications.

Modification of epoxy resins and dispersing methods were extensively studied, which includes the advancement of epoxy
resin by an aromatic amino-carboxylic acid\textsuperscript{12}, esterification of epoxy group by a phosphoric acid\textsuperscript{11}, grafting of acrylics to epoxy resin\textsuperscript{8,10}, transesterification of epoxy resin and acrylic resin\textsuperscript{11}, to make the epoxy resin self-emulsifying and an aqueous powder suspension\textsuperscript{13,14} was also proposed. Among them, the acrylic modified epoxy resins are widely used for the interior coating of DWI cans by spray application\textsuperscript{8,15-17}.

Robinson\textsuperscript{9} concluded that, "It was a simple experiment to pre-form the two resins, epoxy resin and acrylic resin, separately from each other and blend them. If dissolution in a water/amine mixture led to an acceptable dispersion, then it could reasonably be concluded that grafting was not important in the composition. Such blending of separate components was totally unsuccessful and, accordingly, it was concluded that grafting had to take place in order to produce a satisfactory dispersion." Thus, they established the first generation for WBCs for can manufacturing.

The development of WBCs for the exterior of DWI cans was relatively easy because the pre-existing technologies on SBCs were applicable for the water soluble resin systems. WBCs for the interior of DWI cans by spray application have been widely utilized for a closed system. However, WBCs for flat roll coating application used to produce three-piece cans and can ends have been difficult to develop. The following reasons are cited which makes it difficult to develop such WBCs;

1) Much higher performances are required for the coatings compared with ones for DWI cans because three-piece cans are mainly used for foods and beverages which need heat processing
such as retort sterilization.

(2) It is hard to obtain the stability of coating materials during the coating operation because of the higher volatility of water. This also makes it difficult to clean-up the facility at the end of the operation.

(3) It was difficult to obtain a flat smooth coated surface by leveling flow.

Despite Robinson's conclusion[9], an extensive study has been carried out in our laboratory to develop a new manufacturing process of WBCs, which includes blending an epoxy/phenolic resin solution with an acrylic resin solution, dispersing them in an

Fig. 1-2 Fractured test pieces of bonded portion of a Toyo Seam Can by tensile test before and after the sterilization process
aqueous medium by phase inversion\textsuperscript{18-26}. By the new process, it has become possible to develop the inherent performances of component resins, \textit{viz.} adhesion performance and so on. The adhesion performance is excellent, stronger than the metal substrate of 0.22 mm thick steel\textsuperscript{[26,27]}, see Fig. 1-2. Thus, the WBC developed here can be used as an adhesion primer for the sideseam bonded cans used for heat-processed foods and beverages.

1-3. Leveling of Coated Wet Films

It is important to obtain a flat smooth surface in order to achieve good appearance and the inherent performance of a coating film. The quality requirements for the leveling properties of industrial coatings are generally high. However, Coyle\textsuperscript{[28]} showed that it is impossible to control the formation of surface ripples, called ribs, during the application process of coatings by the modification of the rheological properties of the coating fluid, if the application speed is in a range acceptable for commercial production. Although he mainly analyzed the reverse roll coating operation and derived the conclusion mentioned above, it is easier to obtain a flat smooth coated surface with a reverse roll coater than a forward roll coater. Even if it is impossible to control the rib formation by a coating altering operation, it is important to obtain a flat smooth coated surface by good coating flow and leveling. To achieve this, studies have been extensively carried out to understand the leveling process and to obtain coatings and paints which possess improved leveling performance\textsuperscript{[29-42]}.

The leveling of coated wet films was first considered by
Patton\textsuperscript{[31]}. He equated the force balance for a rippled surface and derived the flow rate of the coated liquid. His idea was further extended by Rhodes and King\textsuperscript{[33]} and by Wu\textsuperscript{[37]}. However, their findings did not agree with the observed leveling process of the WBCs developed here. The reason for this discrepancy is thought to be because they treated fluids with no volatile components.

On the other hand, Orchard et al.\textsuperscript{[29,30]} derived the following equation for the time-dependence of the amplitude of a sinusoidally rippled fluid film surface about 30 years ago. They thought that the driving force to promote leveling is the hydrostatic pressure gradient in the film caused by surface tension and the free boundary curvature of the film.

\[ a = a_0 \exp(-C_1 t) \]  

(1-1)

where, \( a_0 \) and \( a \) are the initial amplitude and the amplitude of the ripples at time \( t \) after application, and \( C_1 \) is a constant written as follows;

\[ C_1 = \frac{16 \pi^4 \gamma h^3}{3 \eta \lambda^4} \]  

(1-2)

where, \( \pi \) is the ratio of circumference, \( \gamma \) is the surface tension of the fluid, \( h \) is the mean film thickness, \( \eta \) is the viscosity and \( \lambda \) is the wave length of the ripples. To derive this equation, the following assumptions were made;

1. Newtonian flow characteristics
2. Homogeneous and time-independent viscosity
3. Homogeneous and time-independent surface tension
4. Negligible inertial force (creeping flow)
Equation 1-1 was verified experimentally for fluid films with no volatile components\textsuperscript{[42]}. Orchard discussed that the integrated fluidity, \( \int (1/\eta) \, dt \), should be used instead of the fluidity, \( 1/\eta \), if the viscosity is regarded as being a constant throughout the film, and with increasing time and solvent loss\textsuperscript{[30]}. According to the above theory\textsuperscript{[29]}, the higher the surface tension of the coating fluid is, the faster the leveling is expected to proceed. The surface tension of WBCs without any co-solvent tends to be much higher compared with that of the usual SBCs. However, the leveling characteristics of WBC are commonly observed to be inferior and it is quite hard to obtain a flat smooth coated surface by roll coating. However, a great discrepancy was found on the leveling rates of air-drying solution paints, even if time-dependent viscosity was accounted for\textsuperscript{[42]}. Moreover, the coatings with a higher surface tension tend to cause eye-holes because of their poor wetting characteristics, which would not be applied for commercial production.

Many efforts were made to extend the above equation for non-Newtonian fluids\textsuperscript{[32-34,37,39,40]}, and Camina et al.\textsuperscript{[34]} introduced the following equation derived by Murphy\textsuperscript{[35]}:

\[
\frac{da}{dt} = -\frac{N}{2N+1} \left( \frac{\gamma a}{K} \right)^{\frac{1}{N}} \left( \frac{2\pi}{\lambda} \right)^{\frac{2+1}{N}} \cdot h^\frac{2N+1}{N} \tag{1-3}
\]

where, \( N \) is the power constant and \( K \) is the viscosity at 1 sec.\textsuperscript{-1}.

However, their treatments were mostly based on the fluids with no volatile components, and that the viscosity and the

9
surface tension of the fluids were not assumed to change throughout the leveling process, which is not applicable to the thermosetting WBCs discussed here. They tried to extend the theory for fluids with volatile components, and introduced a time-dependent viscosity instead of a constant viscosity, $K$. However, the viscosity and the surface tension were thought to be homogeneous throughout the film independent of the film thickness.

Overdiep derived the following equation\[11\], from the evaluation of the additional term caused by the existence of the surface tension gradient;

$$\frac{da}{dt} = -\frac{C_2}{\eta} \left( a + C_3 \int_0^t a \, d\mu \right)$$

(1-4)

where, $C_2$ and $C_3$ are constants. As the analytical solution to this equation was not known, he used a curve fitting method using the observed data by stepwise computation to find the constants $C_2$ and $C_3$, and compared them with the calculated results. However, the calculated results were not in good agreement with the experimentally observed ones for air-drying decorative paints. He assumed that the driving force to promote leveling is the surface tension gradient arising from the difference in the surface tension between the pure solvent and the pure resin, and the growth of lateral resin concentration gradient produced by the difference in the film thickness and the evaporation of solvents.

He also tried to extend Eq. 1-4 to express the surface wave amplitude ultimately obtained using the concept of "total flow". Although the physical meaning of the total flow was clearly
defined, it is quite doubtful if it can be determined by the proposed methods, see for example his review paper\[41\]. Although the introduction of surface tension gradient into account seems unique, it is impossible to predict the proceedings of the leveling from Eq. 1-4 for well characterized fluids. This diminishes the applicability of his theory.

It is important for WBCs containing a co-solvent to consider the concentration of the co-solvent and the concentration of resins during the leveling process because a small addition of a co-solvent decreases the surface tension of a WBC drastically. In other words, a very sharp surface tension gradient could be developed in the coated wet film during the leveling process by a small amount of solvent evaporation. The leveling process of a three component systems (water, a solvent and a resin) has not been considered so far, although such systems have been widely applied in many industries\[8-19,41-43\]. Overdiep's idea that the surface tension gradient can be one of the primary forces to promote leveling seemed important. Accordingly, the leveling performance was expected to be improved by the addition of such co-solvents which evaporate faster by azeotropic evaporation, because the surface tension of WBCs is lowered by the addition of a co-solvent in most cases and that the concentration of co-solvent at the trough portion of surface ripples is expected to be lower during the drying process. I experimentally verified this idea and succeeded in improving the leveling performance of WBCs\[44\].

Wilson\[45\] analyzed the leveling process of paints using typical rheological values and several evaporation rates. He
got consistent results observed by Overdiep\textsuperscript{[4]}\textsuperscript{[4]}, and the occurrence of the negative amplitude of surface ripples or the reappearance of ripples could be predicted. However, the duplication of his procedure using the experimentally determined values for my WBCs gave inconsistent results with my observation quantitatively.

As noted so far, the mechanism of leveling is not completely understood in terms of formulation and rheological characteristics as yet. In consequence, the improvement of coating characteristics has been totally owed to the skill of experienced formulators. Thus, the theory has been strictly desired to predict the leveling performance of coatings in terms of formulation and their rheological characteristics.

1-4. Flexibility of Cured Films

Besides the adhesion performance, the flexibility and the flavor characteristics is cited to be important for can coatings. It was vaguely believed that the cured films with higher molecular weight of network chain, $M_c$, possess better flexibility. $M_c$ would be characterized using the theory of rubber elasticity, \textit{viz.} the equilibrium swelling\textsuperscript{[46]} and the elastic modulus at a rubbery temperature region\textsuperscript{[47]}. Many studies have been carried out to understand the relationship between the chemical structure and the physical properties of cured epoxy resin systems\textsuperscript{[48-62]}\textsuperscript{[48-62]}. However, smaller values of $M_c$ were usually obtained by the above techniques, which contradicts to the relatively flexible nature of cured epoxy films\textsuperscript{[63]}\textsuperscript{[63]}. Thus, I developed a new procedure to determine $M_c$ using the theory of
partitioning of components between sol and gel proposed by Flory\textsuperscript{[47,48]}. The results obtained were feasible to explain the physical properties of the cured films and the flexibility of the cured films were expressed as a function of $M_c$. Using the above findings, I analyzed the mechanism of crosslinking and found the adverse effects of lower molecular weight components. I experimentally obtained a liquid-liquid extracted epoxy resin, which contains a smaller amount of lower molecular weight components. From the analysis of the cured films including those formulated using the above epoxy resin, I found that the flexibility of cured films can be expressed as a function of $M_c$. By utilizing the above epoxy resin, the optimum flexibility can be achieved with less amount of sol in the cured films. Thus, the flavor aspects can be improved by reducing the sol content at the degree of cure with optimized flexibility\textsuperscript{[41]}. 

1-5. Thesis Scope

The first objective of this study is to develop WBCs which are applicable for three-piece cans, especially those used as an adhesion primer for sideseam bonded cans. SBC epoxy/phenolic coatings have been utilized as the adhesion primer for this purpose since the can was first developed. The key performance is the adhesion strength, stronger than a steel strip of 0.22 mm thickness, see Fig. 1-2. The adhesion structure is so designed as to withstand a severe sterilization process after the cans are filled\textsuperscript{[14]}. 

Toward higher adhesion performances of coatings, many efforts were made\textsuperscript{[1,2,45-48]}. However, these efforts were mainly
paid to improve the performances of SBCs. Therefore, a program was started to develop high performance WBCs for can coating application utilizing the technologies developed for SBCs, and succeeded in developing a new manufacturing process of WBCs, which includes blending an epoxy resin solution with an acrylic resin solution with or without hardeners, followed by neutralization by ammonia or amines [18-21, 79, 80]. This research has concentrated on developing a new emulsification process to manufacture WBCs for cans with optimized combination of dry and wet adhesion using an epoxy resin and a phenol/formaldehyde resole as its hardener [24, 27]. I also examined the factors affecting emulsification stability, the factors affecting adhesion performance [25, 27] and characterized the coatings and their cured film [26, 27]. By the development of the new emulsification process, it has become possible to develop the inherent characteristics of the constituent materials as in the case of SBCs. These findings will be dealt in Chapters 2, 3 and 4.

However, during the process of commercial application of the WBCs, it has become quite important to improve the application characteristics including the leveling, which is the second objective of this study. According to the Orchard's theory [23], the higher the surface tension of the coating fluid is, the faster the leveling is expected to proceed. However, such a coating material would not be applied for commercial production because of their poor wetting characteristics. It was vaguely believed also that the Newtonian flow characteristics is important to improve the leveling performance as in the case
of SBCs.

As noted above, however, Overdiep\(^{[42]}\) suggested that the formation of a surface tension gradient is important to accelerate leveling flow. He suggested that the leveling of coated wet film would be accelerated if the surface tension at the trough portion of the surface ripples is higher compared with that at the crest portion during the drying process by well defined surface tension driven flow\(^{[82-86]}\). This idea was verified experimentally and we succeeded in improving the leveling performance of WBCs.

I constructed an observation system for the leveling process which can distinguish the effects of co-solvent added\(^{[44]}\). The evaporation behavior from the coated surface of WBC was estimated and the change in the viscosity and in the surface tension during drying depending on the initial film thickness\(^{[87]}\) was determined. Thus, the formation of the surface tension gradient and the viscosity gradient during drying were estimated and the empirical relationships to express the formation of the surface tension gradient and the viscosity gradient were derived. On the other hand, leveling experiments under a controlled condition were carried out\(^{[84]}\), because it is well known that the evaporation from WBCs depends on the atmospheric conditions such as temperature, relative humidity and air flow. During the experiments, the film thickness was found to have a significant effect on the leveling behavior of WBCs\(^{[89]}\). Thus, I experimentally determined the effects of film thickness on the leveling behavior. I also compared the results with previous theories and found great discrepancy to apply them for the
thermosetting WBCs\cite{11, 89}. These findings will be dealt in Chapters 5, 6, 7 and 8.

The final objective is to improve the flexibility of the coating films. I developed a new procedure to estimate $M_c$ using the theory of partitioning of components between sol and gel proposed by Flory\cite{47, 64}. This made it possible to evaluate $M_c$ properly in regard to the physical properties of the cured films. Liquid-liquid extracted epoxy resin was experimentally prepared and the $M_c$ and the flexibility of the cured films were determined\cite{65}. Thus, the flavor aspects can be improved by reducing the sol content at the degree of cure with optimized flexibility\cite{65}. These findings will be dealt in Chapters 9 and 10.

\begin{center}
\textbf{Nomenclature}
\end{center}

\begin{itemize}
\item \textit{DWI can} \hspace{0.5cm}: Drawn and wall ironed can
\item \textit{SBC} \hspace{0.5cm}: Solvent borne coating
\item \textit{WBC} \hspace{0.5cm}: Waterborne coating
\item \textit{VOC} \hspace{0.5cm}: Volatile organic compounds
\item \textit{SO}_x \hspace{0.5cm}: Sulfur oxides
\item \textit{NO}_x \hspace{0.5cm}: Nitrogen oxides
\item \textit{CO}_2 \hspace{0.5cm}: Carbon dioxide
\item $a_0$ \hspace{0.5cm}: The initial amplitude of ripples
\item $a$ \hspace{0.5cm}: The amplitude of ripples at time $t$ after application
\item $t$ \hspace{0.5cm}: Decay time after application of coating
\end{itemize}
\( C_i \) : A constant
\( \pi \) : The ratio of circumference
\( \gamma \) : The surface tension of the coated fluid
\( h \) : The mean film thickness
\( \eta \) : Viscosity of the coated fluid
\( \lambda \) : The wave length of the ripples
\( N \) : The power constant
\( K \) : The viscosity of a coating fluid at 1 sec.\(^{-1}\)
\( C_2, C_3 \) : Constants
\( M_c \) : Molecular weight of network chain

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CHAPTER 2. DEVELOPMENT OF EMULSIFICATION PROCESS

2-1. Introduction

As noted in the previous chapter, it is quite important to develop waterborne coatings, WBCs, with superior adhesion performance to be used as an adhesion primer for the side-seam bonded cans. It was considered hopeless to utilize the existing technologies, which include the acrylic modification of epoxy resin by grafting or esterification \(^{(1,2)}\), to achieve such a high level of adhesion performance. On the other hand, the component resins, epoxy resin and phenolic resin (resole), used for the solvent borne adhesion primer are highly tuned to achieve their adhesion performance. The inherent performance of the component epoxy resin was assumed to be degraded by the chemical modification, grafting of acrylcs or trans-esterification of acrylic resin. To avoid the adverse effects introduced by the chemical modification of epoxy resin and to maintain the inherent performance of the component epoxy resin, it was necessary to develop a new emulsification process that did not include the chemical modification of epoxy resin. Such a process would enable the development of the inherent performance of the component resins \(^{(1)}\).

2-2. Emulsification of Epoxy Resin

The epoxy resin used was an experimental grade solid epoxy resin supplied by the Dow Chemical Co. The weight average molecular weight, \(M_w\), of the resin was about 15,500 and the epoxide equivalent weight was about 3,600. Characterization
procedures of the resin have been described elsewhere\(^4\).

The acrylic resin used in this study was prepared by radical polymerization using benzoyl peroxide as an initiator. The polymerization procedure was shown elsewhere\(^2\). Polymerization conditions were controlled so as to obtain a random copolymer of the following monomers. The monomer ratio was methacrylic acid, MAA/methyl methacrylate, MMA/ethyl acrylate, EA/styrene = 40/20/20/20. The acrylic resin was obtained as a solution having 40% non-volatile content, NV, dissolved by a mixed solvent of \(n\)-butanol, \(n\)-BuOH/butyl acetate = 40/20 by weight. \(M_w\) of the resultant polymer was determined to be about 80,000 by gel permeation chromatography, GPC, calibrated using polystyrene standards. The glass transition temperature, \(T_g\), of the polymer calculated from the monomer composition was about 110\(^\circ\)C.

The epoxy resin was dissolved by the mixed solvent of \(n\)-BuOH/butyl acetate/ethylene glycol mono-butyl ether, EGBE = 40/40/20 to give 40% NV solution and 15 parts per hundred resin, PHR, of acrylic resin were added based on the epoxy resin. The mixed solution showed an opaque appearance.

To 1,000 g of the resin mixture, violently agitated in a stainless steel vessel by a Homodisper produced by Tokushu Kika Kogyo Co., Ltd., Osaka, was added 450 g of aqueous ammonia containing 2.0 equivalents, eq., of \(NH_4\) based on the carboxyl group content of the acrylic resin gradually in 50 ml aliquots at 1 minute intervals. Then, 550 g of deionized water was added in the same manner. The emulsification was carried out at an ambient temperature. A water-in-oil, W/O, emulsion was
formed at first by the addition of aqueous ammonia, and then, by
the addition of deionized water, an oil-in-water, O/W, emulsion
was formed by phase inversion.

Electric conductivity during the emulsification process was
monitored using the apparatus shown in Fig. 2-1. This
apparatus includes an electric DC source of 5.0 volts, a platinum
cathode of 3 mm in diameter, a copper anode (5 by 5 mm), a
standard resistance of 1.00 Ω, and a recorder. Electrodes
were placed facing each other at a distance of 10 mm. The
voltage drop between the 1.00 Ω resistor was recorded to monitor
the electric current between the electrodes.

Figure 2-2 shows the change in electric conductivity during
the emulsification process. The electric current was not

---

**Fig. 2-1** Schematics of apparatus to measure electrical current;
A: Copper anode, C: Platinum cathode, E: Electrical
source of 5.0 VDC, R: Standard resistor of 1.00Ω,
Rec.: recorder, H: Holder, Ag.: Agitator, and
V: Emulsification vessel
detected at first, because the continuous phase was composed of the epoxy resin solution and its electric conductivity was low.

At the moment when a certain amount of aqueous ammonia was added, the electric current increased instantaneously, indicating the occurrence of a phase inversion, because the electric conductivity of the aqueous medium is much higher than that of the epoxy resin solution. The increase of electric current was observed after a certain induction period following the addition of aqueous ammonia. The delay was considered to be caused simply by the delay in achieving homogeneity. The electric current recorded increased by further addition of aqueous ammonia and then of deionized water.

Particle size and distribution of the dispersed phase for the resultant O/W emulsions were characterized using a laser light scattering type particle size analyzer Microtrac SPA
produced by Nikkiso Co., Ltd., Tokyo, before and after solvent stripping at an ambient temperature.

*Figure 2-3* shows the particle size distribution in the resultant emulsion. The particle size analyzer employed characterized particles from 0.12 to 42.21 \( \mu m \), by its instrumental restrictions. All particles out of this range were omitted from the data. The omitted portion was determined not to be very great, using a similar particle size analyzer, *Microtrac SRA*, produced by the same company, by which it is possible to characterize larger particles up to 300 \( \mu m \).

![Graph showing particle size distribution pattern of an epoxy emulsion. Mean particle size: 3.11 \( \mu m \)](image-url)

This emulsion contained a significant amount of coarse particles and was not preferable for use as a WBC. However,
the epoxy resin could be emulsified without any chemical modification of the epoxy resin, just by blending by a phase inversion method, because there existed a peak in the distribution in the fine particle size region. The phase inversion of the system occurred instantaneously, which may enable a continuous emulsification process. Therefore, any hydrophobic resin can be emulsified if suitable solvents and compatible dispersants for the resin are found, which widens the design latitudes of formulation and promises the possibility of developing higher performance WBCs.

2-3. Emulsification of Epoxy/Phenolics

An epoxy resin was dissolved in the mixed solvent of n-BuOH/butyl acetate = 50/50 to give 40% NV. The phenol/formaldehyde resole, phenolic resin, used was proprietarily supplied by Toyo Ink Mfg. Co., Ltd., Tokyo, and was derived from p-cresol and bis-phenol A. The phenolic resin was supplied as a solution which contained 40% NV in a mixed solvent of methyl iso-butyl ketone, MIBK/methyl iso-butyl carbinol, MIBC/n-BuOH = 35/35/30. The epoxy resin solution and the phenolic resin solution were mixed at a ratio of epoxy/phenolic = 85/15 in solid base and then precondensed at 110°C for four hours. The 15 PHR acrylic resin solution based on the epoxy/phenolics in solid base was added and the mixture was agitated until homogeneous. Emulsification was carried out as in the case of the epoxy resin solution.

The viscosity change during the emulsification process was monitored using a spiral viscometer PC-ITL manufactured by Malcom
Fig. 2-4  Viscosity change during emulsification process

Fig. 2-5  Volume fraction of dispersed phase during emulsification process
Co., Tokyo, with a B rotor. The shear rate was set at $108 \text{s}^{-1}$ throughout the measurement.

*Figure 2-4* shows the viscosity changes during the emulsification process. The viscosity of the system decreased rapidly at first. At this stage, neutralization occurs and ionized groups are introduced in the acrylic resin. The viscosity of the system may be mainly governed by the amount and nature of the acrylic resin, the largest molecular weight component in the system. The conformation of the acrylic resin may also change to the hard coil or micelle-like one from the relatively extended random coil by the introduction of polar groups and migration of poor solvent, water, which will result in a decrease of viscosity of the continuous phase. Because of the phase inversion, the viscosity of the system increased instantaneously, since the volume fraction of dispersed phase increased by about three fold as shown in *Fig. 2-5*. In this *Figure*, the volume fraction of dispersed phase was plotted against the amount of aqueous ammonia and deionized water, which was calculated assuming that the density of the mixed resin solution phase is 0.80 $\text{g/cm}^3$, and that water and solvents do not dissolve in each other.

*Figure 2-6* shows the particle size distribution of the resultant emulsion. This emulsion had a single peak in its particle size distribution and did not contain any coarse particles larger than 3 $\mu\text{m}$. The mean particle size of this emulsion was slightly larger than that of conventional WBCs [1,2] but much smaller than that of aqueous powder suspensions [5]. The particle size distribution was reasonably narrow and the
largest size of particles was acceptable for use as a WBC.

The solvents in this O/W emulsion were stripped off using a rotary vacuum evaporator to give a 30% by weight NV emulsion, which was used to examine the stability of the resultant products. The mean particle size and particle size distribution did not show any difference when characterized with or without solvents. Stability evaluation at 50°C for one month in a sealed glass bottle revealed that the WBC had excellent stability, i.e., very little change in viscosity, particle size, and appearance.

![Particle Size Distribution](image)

**Fig. 2-6** Particle size distribution pattern of an epoxy/phenolic emulsion. Mean particle size: 0.68 μm

2-4. Effects of (Epoxy/Phenolics)/Acrylics Ratio

The same epoxy/phenolics solution was used to study the
effects of acrylic resin content. The acrylic resin solution was diluted by n-BuOH, MIBK, and MIBC to give the same solvent composition as the epoxy/phenolics solutions. These solutions were blended to give a predetermined ratio, and emulsified by the process described above.

Figure 2-7 shows the influence of acrylic resin content on mean particle size of dispersed phase for the resultant O/W emulsions before stripping the solvents. The mean particle size of the dispersed phase decreased slightly with increasing acrylic resin content. The excess amount of acrylic resin, surfactant, may help to stabilize the emulsification process, although the amount of acrylic resin required to emulsify and to obtain dispersions with fine particle size is relatively small. It was surprising that a stable emulsion could be obtained with only a 3 PHR acrylic resin based on epoxy/phenolics, because

Fig. 2-7 Effect of acrylic resin content on the mean particle size of the dispersed phase
conventional dispersion type WBCs, aqueous dispersions of acrylic modified epoxy resin, contain 20 to 40 PHR acrylic components so as to obtain stable dispersions\[1,2,4\].

Although emulsions with less acrylic resin produced a larger particle size, it was confirmed possible to produce emulsions with a fine particle size by precise control of the emulsification process. The reduction of acrylic resin incorporated will help to develop excellent performance of epoxy resin and its hardeners, because the influence of acrylic resin can be minimized. However, the acrylic resin content should be adjusted so as to give excellent emulsification stability, preferable rheological properties for application, and also excellent film performance.

2-5. Effects of Solvents

Water soluble solvents such as EGBE are widely used in the coating industry because they dissolve epoxy resin and other resins used as film forming components very well, and solvents that dissolve both epoxy/hardener mixtures and acrylics should be chosen for the present emulsification process. However, the epoxy resin solution in EGBE could not be emulsified. The aqueous ammonia added was dissolved in the epoxy resin solution, and did not form a dispersed phase as in a W/O emulsion. Thus, the resin solution became highly viscous, perhaps because the EGBE/aqueous ammonia mixture dissolved the acrylic resin very well and finally formed a separate phase with water. In such cases, it is not possible to emulsify the system.

It seems preferable to use water insoluble solvents for
emulsification, because some water soluble solvents such as EGBE have adverse effects on emulsification as mentioned above. Therefore, it is worthwhile to examine the effects of solvents, to find which solvents show adverse effects on emulsification. These experiments were concentrated to determine the amount of water soluble solvents acceptable for this process. For this purpose, a series of emulsification experiments were carried out using a resin mixture of epoxy/phenolic/acrylic (85/15/15) dissolved in a series of mixed solvents which included EGBE.

First, solid epoxy resin and phenolic resin solutions were charged into a four necked flask at the predetermined ratio in solid base. Next, a mixed solvent of a predetermined amount of EGBE and butyl acetate was added so as to give the 40% NV solutions of epoxy/phenolics. The agitated mixture was heated to the boiling temperature of n-BuOH to dissolve epoxy resin, cooled to 110°C, kept at the temperature for four hours and then cooled to ambient temperature. An acrylic resin solution was added and mixed with the epoxy/phenolics solution at a predetermined ratio. At this stage, the mixture contained MIBK, MIBC, n-butanol, EGBE, and butyl acetate. Emulsification experiments were carried out as described above.

The results are shown in Table 2-1, where the mean particle size of dispersed phase in the resultant emulsions was also cited for the cases in which emulsification was successful. Emulsification became difficult when the EGBE content in the mixed solvent exceeded 45%. In cases when the EGBE content was 45% or more, an oily component was formed in the resultant emulsion, which was a part of the resin solution that failed to
form dispersed particles.

Both water and water soluble solvents may be distributed in both the aqueous and the resin solution phases. To determine the distribution of water and water soluble solvents, an additional experiment was carried out. A mixture of mixed resin solution of epoxy/phenolics (50g) and deionized water (50g) was shaken violently in a plastic bottle, and then centrifuged to separate out the aqueous phase.

As in the case of emulsification experiments, an oily component was formed when the EGBE content was 45% or more, see the photograph Fig. 2-8. For the samples with 45 and 50% EGBE, the mixtures were separated into three phases. The upper phase was the phenolic resin solution of the mixed solvents, the middle phase was aqueous medium in which a small amount of solvent was dissolved, and the lower phase was resin solution of mainly epoxy resin and acrylic resin in which a small amount of water was dissolved. In the cases with an EGBE

<table>
<thead>
<tr>
<th>Solvents EGBE/Others</th>
<th>Emulsification</th>
<th>Mean Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>+</td>
<td>0.90</td>
</tr>
<tr>
<td>10/90</td>
<td>+</td>
<td>0.81</td>
</tr>
<tr>
<td>25/75</td>
<td>+</td>
<td>0.56</td>
</tr>
<tr>
<td>35/65</td>
<td>+</td>
<td>0.85</td>
</tr>
<tr>
<td>40/60</td>
<td>+</td>
<td>0.88</td>
</tr>
<tr>
<td>45/55</td>
<td>-</td>
<td>----</td>
</tr>
<tr>
<td>50/50</td>
<td>-</td>
<td>----</td>
</tr>
</tbody>
</table>
content at 40% or less, the mixture was separated into two phases. However, their composition was different depending on the EGBE content. When the EGBE content was 25, 35, and 40%, the upper phase was the aqueous phase and the lower phase was the resin solution in which a small amount of water was dissolved. On the other hand, when the EGBE content was 10% or lower, the upper phase was a resin solution and the lower phase was an aqueous phase. It is assumed that the resin solution does not dissolve much water when the EGBE content is low, and the density of the resin solution phase is lower than that of the
aqueous phase.

The mechanism of phase separation is not well understood. However, the resin solution in hydrophobic solvents was preferable for obtaining an emulsion with fine particle size.

2-6. Effects of the Monomer Composition of the Acrylic Resin on Emulsification and Adhesion Performance

The monomer composition of the acrylic resin employed as a surfactant may be important in view of emulsification stability and also adhesion performance. The acrylic resin must possess some compatibility with the epoxy/phenolics and also carboxyl functionality to be neutralized in order to emulsify the resin mixture. On the other hand, adverse effects of the acrylic resin on adhesion performance should be avoided.

A series of acrylic resin was prepared using various monomer compositions (see Fig. 2-9). The ratio of MMA and EA was set to be equal, i.e., MMA/EA = 1/1. The molecular weight of these polymers was controlled at around 80,000.

From the emulsification experiments and the evaluation of the resultant emulsions as WBCs, these acrylic resins were classified into three categories; (1) both the emulsification stability and adhesion performance of resultant WBC are good, (2) the emulsification stability is good, but the wet adhesion is poor, and (3) the emulsification stability is poor so a stable WBC was not obtained. Styrene rich systems and EA+MMA rich systems tended to show poor emulsification stability. This may be because the surface activity of the acrylic resin is reduced because of their low carboxyl functionality and/or that
the compatibility with the epoxy/phenolics is reduced. On the other hand, wet adhesion tended to decrease for the systems with a high MAA content. This is assumed to be because the hot-water resistance of the cured films is reduced by the introduction of too much carboxyl functionality.

Thus, for the epoxy/phenolics used in this study, a preferable monomer composition of acrylic resin was found and used throughout the study. However, minor adjustments will need to be made for different resin systems.

Fig. 2-9 Effects of the monomer composition of the acrylic resin on the emulsion stability and adhesion performance. Marks denote: ○: good adhesion, good emulsion stability, □: inferior adhesion, good emulsion stability, and ▲: inferior emulsion stability.
2-7. Continuous Emulsification

Based on the results shown above, a scaled-up, continuous emulsification was tried using a mixed resin solution of epoxy/phenolic/acrylic = 85/15/15. The resin solution was prepared to be 40% NV by weight. The main solvents incorporated were n-BuOH and butyl acetate, and contained a small amount of MIBK and MIBC.

Figure 2-10 shows the flow chart of the emulsification system. The system consisted of two agitation units, pumps, supply tanks, and a reservoir. The agitation unit used was T.K. Homomic Line Flow model 100 manufactured by Tokushu Kika Kogyo Co., Ltd., Osaka. The agitation unit was very compact and agitated efficiently. It also worked under pressure, which helped to control cavitation and to improve agitation efficiency.

Fig. 2-10 Schematic diagram of the continuous emulsification apparatus

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Tank 1 was charged with 23 kg of the mixed resin solution, tank 2 with 7.2 kg of deionized water and 0.8 kg of 25% aqueous ammonia, and tank 3 with 15 kg of deionized water. The flow rate of pumps was adjusted to be 1.00 kg/min (Pump 1), 0.45 kg/min (Pump 2), and 0.55 kg/min (Pump 3), respectively, and agitation was started. The products obtained in the first few minutes were disposed of, until a stable emulsion was obtained continuously. The gauge pressure in the agitation units was controlled to be 0.12 MPa (1.2 kg/cm²) throughout the operation.

The mean particle size of the dispersed phase was determined to be 0.56 μm, both before and after solvent removal. Stability of the stripped emulsion was tested and no practical changes were observed in mean particle size, viscosity, and appearance after one month storage at 50°C.

Thus it became possible to emulsify the epoxy resin and its hardener continuously with a minimum amount of acrylic resin, without any chemical modification of the epoxy resin.

2-8. Concluding Remarks

A new manufacturing process of waterborne coatings, WBCs, was established, which included blending an epoxy resin solution and an acrylic resin solution with or without hardener, followed by neutralization of carboxyl group in the acrylic resin by ammonia or an amine, and emulsification by phase inversion. This process was considered to be useful to maintain the excellent performance of the component epoxy resin and its hardener, because the epoxy resin is not chemically modified and the amount of acrylic resin as a surfactant is minimized.
Factors affecting the stability of emulsification and resultant emulsion were studied, namely the amount of acrylic resin and hydrophilic solvents. The minimum amount of acrylic resin required to emulsify the epoxy resin was found to be relatively small, and the use of hydrophilic solvents should be minimized to stabilize the emulsification process. It is assumed that the added water dissolved in the resin solution when an excess amounts of hydrophilic solvents was employed, and would not form dispersed particles, resulting in gelation of the system. The phase inversion of the system occurred instantaneously when sufficient water was added in the cases with a small hydrophilic solvent content, and emulsification was successfully carried out.

On the basis of the results mentioned above, a continuous emulsification process was established, which would enable a stable emulsification process for WBC manufacturing and possibly a reduction in emulsification cost.

**Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBC</td>
<td>Waterborne coatings</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>$MAA$</td>
<td>Methacrylic acid</td>
</tr>
<tr>
<td>$MMA$</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>$EA$</td>
<td>Ethyl acrylate</td>
</tr>
<tr>
<td>$NV$</td>
<td>Non-volatile content</td>
</tr>
<tr>
<td>$n$-$BuOH$</td>
<td>$n$-Butanol</td>
</tr>
<tr>
<td>$GPC$</td>
<td>Gel permeation chromatography</td>
</tr>
</tbody>
</table>
\[ T_g \] : Glass transition temperature

\[ \text{EGBE} \] : Ethylene glycol mono-butyl ether

\[ \text{PHR} \] : Parts per hundred resins

\[ \text{W/O emulsion} \] : Water-in-oil emulsion

\[ \text{O/W emulsion} \] : Oil-in-water emulsion

\[ \text{MIBK} \] : Methyl iso-butyl ketone

\[ \text{MIBC} \] : Methyl iso-butyl carbinol

References


CHAPTER 3. FACTORS AFFECTING ADHESION PERFORMANCE

3-1. Introduction

The WBCs developed here are designed to develop the optimized balance of dry and wet adhesion as noted in the previous section. Therefore, to avoid the adverse effects of the acrylic resin used as a surfactant, only a minimum amount of resin should be used. On the other hand, if its adverse effects on the adhesion performance are negligible, then the amount of acrylic resin can be adjusted to achieve an optimum balance of emulsification stability and application easiness.

The pH value of deionized water or an aqueous dispersion tends to decrease during storage because of the absorption of carbon dioxide. This should be avoided to insure stability of the emulsion when an anionic surfactant is employed. To keep the system in the basic region, it is a common practice to add some amines. Some amines may react with epoxy resin at the baking process\(^1\), which should be avoided to achieve ultimate adhesion performance of epoxy resin crosslinked by phenolic resin\(^2\). Furthermore, crosslinking of epoxy resin by some amines occurs at relatively low temperatures\(^3\), which may cause degrading of adhesion performance during storage. Thus, a systematic study was carried out to determine the effects of acrylic resin content, neutralizer and stabilizing amines on the adhesion performance of the resultant WBC.

3-2. Effects of Acrylic Resin Amount

To study the effects of the acrylic resin amount on adhesion
performance, six WBCs were prepared with different amounts of acrylic resin, ranging from 3 to 30 PHR, based on solid epoxy/phenolics resin. WBCs were evaluated as follows.

WBCs were coated, using a #8 coating bar, on tin free steel, TFS (Toyo Kohan Co., Ltd., Tokyo), an electro-chemically surface-treated steel that has a layer of chromium oxide on the surface and a layer of metallic chromium between the steel substrate and the chromium oxide layer. The coated panel was baked in a gas forced air oven at 185°C for 12 min and then at 215°C for 12 min to give a dry film thickness of about 2 μm.

All adhesion data were obtained by the T-peel test (ASTM D1876-72) using an Instron type tensile tester. The T-peel test strips were prepared by first cutting the coated and cured TFS panel into 5 mm wide strips. Next, a 40 μm thick strip of thermoplastic adhesive supplied by Toray was placed between two panel strips with the coatings facing the adhesive. Each unit was then heat bonded under a pressure of 25 kPa at a temperature of 200°C for 30 s. The panels were then tested for dry adhesion using the tensile tester for a T-peel test. Wet adhesion was measured in the same manner after the test specimen was soaked in 90°C water for four days.

The gel content was measured by means of methyl ethyl ketone, MEK, extraction. Coated and cured TFS panels were first cut into 4 by 15 cm strips and weighed, \( W_1 \). Next, the specimens were soaked in boiling MEK for one hour, rinsed with MEK, dried in an electric forced air oven at 200°C for 10 min and weighed, \( W_2 \). Each sample was then soaked in concentrated sulfuric acid for 5 min to remove the coating film from the
substrate, rinsed, dried, and weighed, \( W_j \), again. The gel content was calculated from the following equation:

\[
Gel\ Content = \frac{(W_g - W_j)}{(W_i - W_j)} \times 100
\]  

(3-1)

Table 3-1 shows the mean particle size of the dispersed phase for each WBC along with dry film gel content and adhesion. The mean particle size of the dispersed phase of WBCs with a lower acrylic content tends to be larger than that of the WBCs with a higher acrylic resin content. However, even in such cases, no oily component in the emulsion was found just after emulsification, which suggests that the emulsification was successfully carried out and that it would be possible to obtain a fine emulsion by precise control of the emulsification process, as described in the previous section.\(^4\)

Little influence of the acrylic resin content on the gel

Table 3-1  Effects of acrylic resin content on the mean particle size of the dispersed phase of emulsions, the gel content of cured films and the adhesion properties

<table>
<thead>
<tr>
<th>Acrylic Resin Content (PHR)</th>
<th>Mean Particle Size (( \mu m ))</th>
<th>Gel Content (%)</th>
<th>Dry Adhesion (kg/5mm)</th>
<th>Wet Adhesion (kg/5mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.69</td>
<td>72.2</td>
<td>5.5</td>
<td>4.7</td>
</tr>
<tr>
<td>5</td>
<td>1.93</td>
<td>72.6</td>
<td>5.5</td>
<td>3.9</td>
</tr>
<tr>
<td>10</td>
<td>0.86</td>
<td>73.2</td>
<td>5.4</td>
<td>4.2</td>
</tr>
<tr>
<td>15</td>
<td>0.70</td>
<td>74.6</td>
<td>5.4</td>
<td>4.3</td>
</tr>
<tr>
<td>20</td>
<td>0.83</td>
<td>76.5</td>
<td>5.7</td>
<td>4.4</td>
</tr>
<tr>
<td>30</td>
<td>0.65</td>
<td>77.6</td>
<td>5.7</td>
<td>4.0</td>
</tr>
<tr>
<td>None</td>
<td>----</td>
<td>81.2</td>
<td>5.5</td>
<td>3.9</td>
</tr>
</tbody>
</table>

(None : Solvent borne counterpart)
content was observed. The molecular weight of the acrylic resin was much higher than that of the epoxy resin or the phenolic resin, which seemed to help the acrylic resin to form an insoluble network structure. Because of the reduction of the hardener (phenolic resin) concentration in the resin mixture, a slight reduction of the gel content was observed by an increase in the acrylic resin content.

Dry and wet adhesion of WBCs was excellent, even better than the solvent-borne counterpart in many cases. However, the wet adhesion at a higher acrylic resin content tended to be lower, possibly because of the introduction of the hydrophilic acrylic component. Thus, the acrylic resin content should not be too high in order to obtain the ultimate adhesion performance. In other words, the lower the acrylic resin (surfactant) content, the better was the adhesion. The acrylic resin content should be selected to achieve the optimum balance of adhesion performance and easiness of emulsification and application.

3-3. Effects of Neutralizer

To study the effects of the neutralizer, the acrylic resin content was held constant at 15 PHR based on the epoxy/phenolics. A variety of amines were used as the neutralizer, see Table 3-2.

Water/amine mixtures were prepared by dissolving the amines in 450 g of deionized water at a level to give 2.0 equivalents of amine per carboxyl groups in the acrylic resin. Emulsification and stripping procedures employed were the same as described in the previous chapter.

It was possible to produce an emulsion independent of
neutralizer. However, the gel content of the cured film and the adhesion performance was dependent on the neutralizer, see Table 3-2. Wet adhesion tended to be lower in such WBCs with a gel content higher than that of the solvent borne counterpart, see also Table 3-1.

Amines are classified as a hardener for epoxy resins. In fact, when an ethylene glycol mono-butyl ether solution of an epoxy resin was mixed with ammonia and stored in a sealed glass bottle, gelation of the system was observed. Thus, it would be reasonable to assume that some amines work as a hardener for

<table>
<thead>
<tr>
<th>Amines</th>
<th>Gel Content (%)</th>
<th>Dry Adhesion (kg/5mm)</th>
<th>Wet Adhesion (kg/5mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-methyl amine</td>
<td>84.8</td>
<td>7.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Di-methyl amine</td>
<td>89.1</td>
<td>8.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Tri-methyl amine</td>
<td>93.8</td>
<td>5.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Mono-ethyl amine</td>
<td>81.6</td>
<td>6.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Di-ethyl amine</td>
<td>82.5</td>
<td>6.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Tri-ethyl amine</td>
<td>92.0</td>
<td>7.6</td>
<td>3.2</td>
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<tr>
<td>n-Propyl amine</td>
<td>80.8</td>
<td>6.7</td>
<td>3.7</td>
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<td>i-Propyl amine</td>
<td>80.2</td>
<td>6.8</td>
<td>5.8</td>
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<tr>
<td>n-Butyl amine</td>
<td>89.2</td>
<td>7.0</td>
<td>3.3</td>
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<tr>
<td>sec.-Butyl amine</td>
<td>82.6</td>
<td>6.7</td>
<td>5.0</td>
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<tr>
<td>tert.-Butyl amine</td>
<td>83.0</td>
<td>6.5</td>
<td>4.9</td>
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<tr>
<td>Morpholine</td>
<td>79.8</td>
<td>6.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>83.8</td>
<td>6.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Di-methyl amino-ethanol</td>
<td>90.2</td>
<td>4.9</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 3-2 Effects of neutralizer on gel content of cured film and adhesion properties. Baked at 185°C, 215°C, and then 170°C for 12 minutes each.
epoxy resin at the stoving condition, which results in the increase of gel content. We do know whether the adhesion performance of epoxy coatings crosslinked by an amine is inferior compared to epoxy coatings crosslinked by a phenolic resin. This is the reason why epoxy/phenolic coatings are widely utilized as an adhesion primer for sideseam bonded cans. To achieve superior adhesion performance, the occurrence of amine crosslinking should be avoided by the selection of proper amines. The difference in the gel content produced by different amines used as a neutralizer helps to select the proper amine. The best balance of dry and wet adhesion was obtained by the use of ammonia, amines with branched alkyl groups such as iso-propyl amine, sec-butyl amine, and tert-butyl amine or cyclic amines such as morpholine. Ammonia might not work as a hardener probably because of its fast evaporation at the stoving condition and the reactivity of amines with branched alkyl groups or cyclic amines may be much lower because of steric hindrance.

3-4. Effects of Stabilizing Amines

Ammonia and morpholine were selected as the stabilizing amines because they had no adverse effects when used as a neutralizer. Various levels of stabilizing amines were added to the WBC prepared with 10 PHR of acrylic resin and the mixtures were stored at an ambient temperature and at 50°C in sealed glass bottles. The appearance, gel content of the cured film and adhesion performance were checked periodically.

Figures 3-1 and 3-2 show the results. At the higher level of ammonia, the gel content of the cured film gradually
increased with storage, which suggests that crosslinking proceeded under storage conditions. On the other hand, the gel content of the cured film did not increase as much in WBCs with lower levels of ammonia or morpholine. Dry adhesion was not influenced by the change of gel content. However, wet adhesion decreased with increasing gel content, which is assumed to be the result of amine crosslinking. Coagulation of dispersed particles was also observed for WBCs with higher levels of ammonia after storage for one month at 50°C.

Thus, it was concluded that only a minimum amount of stabilizing amines should be added to obtain optimum storage stability, and that an alkyl-branched amines, cyclic amines or ammonia should be used.

3-5. Concluding Remarks

Balanced dry and wet adhesion is required for can coatings, especially when used as an adhesion primer for sideseam bonded cans. A new manufacturing process of high performance, waterborne coatings has been developed to achieve this goal, and the influences of neutralizers, stabilizing amines, and the amount of acrylic resin used as a surfactant on adhesion performance were studied.

Epoxy/phenolics with excellent adhesion performance were developed and little adverse effect of acrylic resin on adhesion was observed, even when excess amounts of acrylic resin were incorporated. On the other hand, the selection of neutralizer or stabilizing amine was critical to achieve an excellent wet adhesion. Amines with branched alkyl groups, cyclic amines
Fig. 3-1 Effects of the stabilizing amine on the gel content of the cured film and the adhesion performance when the emulsions were stored at 25°C. Marks denote; □: none stabilizing amine, +: 0.5 eq. of ammonia per carboxyl group in the acrylic resin, ○: 1.0 eq. of ammonia, ▲: 0.2 eq. of morpholine, ×: 0.4 eq. of morpholine, and ▼: 1.0 eq. of morpholine.
Fig. 3-2 Effects of the stabilizing amine on the gel content of the cured film and the adhesion performance when the emulsions were stored at 50°C using the same marks as in Fig. 3-1
or ammonia were preferable as a neutralizer or stabilizing amine, because they were found to have no adverse effects on wet adhesion. This was assumed to be because these amines and ammonia did not work as a curing agent for the epoxy resin because of their poor reactivity or quick evaporation at stoving conditions, which helped the curing reaction to proceed between the epoxy resin and the phenolic resin as in the case of solvent borne coatings. Contrarily, in many cases when other amines were used, an increase of gel content in the cured coating film was observed, which suggests the occurrence of a curing reaction between the epoxy resin and the amine used as a neutralizer. This is concluded to be the reason why the inherent adhesion performance of epoxy/phenolic coatings cannot be optimized in such cases.

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBC</td>
<td>Waterborne coatings</td>
</tr>
<tr>
<td>PHR</td>
<td>Parts per hundred resins</td>
</tr>
<tr>
<td>TFS</td>
<td>Tin free steel</td>
</tr>
<tr>
<td>MEK</td>
<td>Methyl ethyl ketone</td>
</tr>
</tbody>
</table>

References


CHAPTER 4. CHARACTERIZATION OF COATINGS AND CURED FILM

4-1. Introduction

As has already been shown, the amount of acrylic resin necessary for emulsification is relatively small, and the addition of excess amounts of acrylic resin made it easy to obtain dispersions with a fine particle size\(^1\). Furthermore, the adhesion performance was not affected by an excess amount of acrylic resin\(^2\). However, it is important to know where such acrylic resin exists, in the dispersed particles or in the aqueous medium, in order to understand the morphology of the cured film. Thus, the aqueous phase in the waterborne coating, WBC, was characterized using ultra-centrifugation and gel permeation chromatography, GPC.

On the other hand, the interface between the substrate and the cured coating film was characterized by infrared, IR, spectroscopy after decomposing the epoxy/phenolic component by concentrated sulfuric acid. The structure of the cured film was observed by a transmission electron microscope, TEM, using a sliced and stained sample. Together with the results of mechanical and thermal analysis, the cured film was found to have a unique morphology, which contributed to the development of the new WBC with excellent adhesion performance.

4-2. Characterization of the Water-Soluble Components

The WBC was centrifuged to separate the dispersed particles from the aqueous medium using an ultra-high gravity centrifuge. A clear aqueous solution was obtained at the top of the sample
tube. The non-volatile content in the aqueous solution was analyzed to determine the ratio of polymer in the particles (or on the particles) vs. polymer in aqueous medium. The amount of polymer in the aqueous phase was equivalent to that of the acrylic resin added to the system. If all the acrylic resin is dissolved in the aqueous phase, and no acrylic resin covers the dispersed particles, it is peculiar that a stable dispersion is obtained.

The polymers in the aqueous phase were further analyzed by GPC. At first, hydrochloric acid was added to the aqueous solution to convert the ammonium salt of acrylic acid to its acid and then it was dried. The dried residue was then dissolved by tetrahydrofuran, THF, and filtered to remove the ammonium chloride. The solution was characterized by means of GPC. Figure 4-1 shows the results. Two peaks were observed on the

![Figure 4-1 GPC pattern of the water soluble component](image)

*Fig. 4-1 GPC pattern of the water soluble component*
These fractions were further analyzed by IR spectroscopy. The higher molecular weight fraction corresponded to the acrylic resin and the lower molecular weight fraction to the phenolic resin. Comparison of the peak areas revealed that 90% of the polymer in the aqueous medium was acrylic resin. Because the amount of polymer dissolved in the aqueous medium is equivalent to the amount of acrylic resin added as noted above, it was concluded that 90% of acrylic resin added is dissolved in the aqueous medium and the rest exists with the dispersed particles. It is obvious that the dissolved acrylic resin does not work as a surfactant. Thus only a minor amount of the acrylic resin is assumed to exist with the dispersed particles and cover the particles to stabilize them. The amount of the phenolic resin dissolved in the aqueous medium is smaller compared to the total amount employed. The dissolved phenolic resin seems to work as a hardener for the acrylic resin, as discussed below.

4-3. Characterization of Interface Layer between Substrate and Cured Coating Film

As noted above, the majority of the acrylic resin added was dissolved in the aqueous, continuous phase, and the rest covers the dispersed particles to stabilize them. Then, an acrylic polymer is presumed to exist in the interface between the substrate and the epoxy/phenolic polymer when WBCs are coated and baked.

The WBC was coated on a tin free steel, TFS, panel using a #12 coating bar to give a dry film thickness of about 5 μm.
The coated panels were baked in a gas forced air oven at 215°C for 12 min.

The interface layer was analyzed by IR spectroscopy as follows; the coated and baked TFS panel was immersed in concentrated sulfuric acid for 5 minutes to decompose the epoxy/phenolic polymer but not the acrylic polymer, rinsed with water, dried, and analyzed by IR. The film of the substance remaining on the substrate was too thin to determine its thickness. Figure 4-2 shows the IR spectrum of the organic substance remained on the TFS surface. The spectrum is characteristic of the acrylic resin employed here, although trace amounts of epoxy resin were also found. Thus, the acrylic resin is confirmed to exist at the interface between the substrate and the epoxy/phenolic polymer after the WBC is baked.

![IR spectrum of the organic substance remaining on the TFS surface after removing the epoxy/phenolic polymer by decomposition using concentrated sulfuric acid](image)

*Fig. 4-2* IR spectrum of the organic substance remaining on the TFS surface after removing the epoxy/phenolic polymer by decomposition using concentrated sulfuric acid
This conclusion can be expected from the fact that some of the acrylic resin is dissolved in the aqueous, continuous phase, and the epoxy resin is not.

The above findings suggest that the substance which is in contact with the substrate is the acrylic polymer and not epoxy/phenolic polymer. In the case of standard solvent borne coatings, the epoxy/phenolic polymer is in contact with the substrate and shows excellent adhesion performance. However, in the new WBCs, the adhesion to the substrate is presumed to be totally due to the acrylic resin, and epoxy/phenolic polymer may play the role of improving the cohesive strength of the film.

4-4. Observation of Surface and Cross-Section of the Cured Film

The surface of coated film was observed by TEM using the double stage replica method (Fig. 4-3), which is compared with the photograph for a conventional WBC (Fig. 4-4). It is clearly demonstrated that the surface of coated film with a dispersion type WBC is not flat and smooth, even when coated with a conventional WBC with a fine particle size. The size of the island phase for the conventional WBC is similar to that of the dispersed particles. However, the size of the island phase for the new WBC is much larger than the size of the dispersed particles, see Fig. 4-5 which shows the TEM image of the dispersed particles for the new WBC. This is assumed to be because the dispersed particles are flattened during the precipitation and baking process.

To analyze the cross-section of the cured film, the WBC was
Fig. 4-3 TEM image of the cured film surface of the new waterborne coating

Fig. 4-4 TEM image of the cured film surface of a conventional waterborne coating
Fig. 4-5 TEM image of the dispersed particles of the new waterborne coating

Fig. 4-6 TEM image of the cross-section of a cured film of the new waterborne coating
coated on a tin plate panel using a #30 coating bar to give a dry film thickness of about 20 μm and baked. The dry film was peeled off from the substrate using mercury to form amalgam with tin and to fluidize the tin layer.

Figure 4-6 shows the TEM image for a cross-section of the cured film. The cured film was cut perpendicular to the film plane by an ultra-microtome and stained by ruthenium tetroxide. As can be seen, the acrylic component (bright portion) forms a separate phase from the epoxy/phenolic component (dark portion). However, it is not clear if the acrylic component forms a continuous phase or not. Moreover, it seems as if the epoxy/phenolic component forms the continuous phase, combining the fused particles of the epoxy/phenolic resin by the baking operation. The acrylic component, covering the particles or dissolved in the aqueous medium, are assumed to have gathered together and form a dispersed phase of the acrylic polymer.

4-5. Mechanical and Thermal Properties

Cured free films of the WBC were analyzed by a mechanical spectrometer, Orientec Corp. (formerly Toyo Baldwin) Rheovibron DDV-II-EA at 110 Hz. Figure 4-7 shows the results of the characterization for a new WBC. Two shoulders were observed on the storage modulus, $E'$, data, which suggests the existence of two separate components. This is consistent with the TEM observation (Fig. 4-6).

The storage modulus of the new WBC is compared with that of a solvent borne counterpart with the same epoxy/phenolic composition without acrylics and of a conventional WBC with a
Fig. 4-7 Temperature dependence of dynamic storage modulus ($E'$: ○), loss modulus ($E''$: □), and loss tangent ($\tan \delta$: \bigtriangleup) for the new waterborne coating.

Fig. 4-8 Temperature dependence of dynamic storage modulus ($E'$) for the new waterborne coating (○), a conventional waterborne coating (△), and the solvent borne counterpart (●).
different composition in Fig. 4-8. Both the conventional WBC and solvent borne counterpart possess only one shoulder, which suggests that the structure is homogeneous, even though a hybrid polymer is employed for the conventional WBC.

From the comparison of these findings with those obtained on the solvent borne counterpart, the shoulder in the lower temperature region is thought to correspond to the epoxy/phenolic polymer and in the higher temperature region to the acrylics. Thus, the unique morphology of the new WBC is again demonstrated.

The cured film was further analyzed by a thermo-mechanical analyzer, Rigaku Thermoflex TAS 200 TMA 8140C, by a penetration technique. Figure 4-9 shows the results of the evaluation, with the results of the solvent borne counterpart for comparison.

Two shoulders were observed for the cured film of the new WBC,
Figure 4-10 shows the results of differential scanning calorimetry, DSC, measurements for the new WBC, the solvent borne counterpart and a conventional WBC, using a Perkin-Elmer DSC-2C at a heating rate of 10 °C/min. Unlike the findings obtained by TEM and dynamic mechanical characterization, only a single transition was observed for each sample. The \( T_g \) value for each sample shown in the Figure is the onset temperature of glass transition. The findings obtained for the conventional WBC was consistent with those reported elsewhere\(^{[3]}\).

To understand the reason for this discrepancy, additional experiments were carried out, i.e., DSC measurement using more
samples and at a lower heating rate, for a more precise analysis. However, unexpectedly the signal of $T_g$ for the acrylic component was equivalent to the level of noise and it was difficult to determine the $T_g$ of the acrylic component in the cured film. The $T_g$ for acrylic component determined by the dynamic mechanical measurement was much higher than that estimated by the monomer composition, about 110 °C. $T_g$ is known\(^4\) to increase upon the introduction of crosslinking. If crosslinking is introduced into the acrylic resin, the phenolic resin is assumed to play the role of crosslinking agent. To confirm this assumption, an additional experiment was carried out. Phenolic resin solution was added to the acrylic resin solution at a predetermined ratio, coated and baked at 215 °C for 12 min. Table 4-1 shows the results of $T_g$ measurements by DSC. The $T_g$ values scattered around 150 °C were independent of the phenolic resin content.

However, hot water resistance of the coating film, i.e., blushing by retort sterilization in an autoclave at 130 °C for 30 min, showed pronounced differences; coating film without the phenolic resin showed severe blushing, whereas those with phenolic resin showed no blushing. The coated panels were soaked in boiling methyl ethyl ketone for 30 min to determine the gel content. The coated film of acrylic polymer without the phenolic resin dissolved completely; whereas the films with the phenolic resin remained on the substrate and showed a gel content around 90%.

Thus, the crosslinkage was confirmed to be introduced into the acrylic resin, and that phenolic resin dissolved in the
Table 4-1  Tg of acrylic resin/phenolic resin mixture baked at 215°C for 12 minutes

<table>
<thead>
<tr>
<th>Phenolic Resin Content (%)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>150.4</td>
</tr>
<tr>
<td>1</td>
<td>152.7</td>
</tr>
<tr>
<td>3</td>
<td>148.7</td>
</tr>
<tr>
<td>5</td>
<td>148.1</td>
</tr>
<tr>
<td>7.5</td>
<td>150.4</td>
</tr>
<tr>
<td>10</td>
<td>149.9</td>
</tr>
<tr>
<td>15</td>
<td>151.6</td>
</tr>
<tr>
<td>20</td>
<td>148.8</td>
</tr>
<tr>
<td>25</td>
<td>149.6</td>
</tr>
</tbody>
</table>

aqueous medium reacted with the acrylic resin when baked. The brittle nature of the acrylic resin may also be reduced by the introduction of crosslinking to give a tough film, which helps to improve the adhesion performance at the interface layer between the substrate and the epoxy/phenolic polymer.

4-6. Concluding Remarks

The acrylic polymer and epoxy/phenolic polymers were confirmed to exist in separate phases; the epoxy/phenolic polymers formed a continuous phase and the acrylic polymer formed a dispersed phase in the cured film of the new WBC produced by the phase inversion method, different than the conventional acrylic modified epoxy resin systems. The epoxy/phenolic resins were also confirmed to form spherical particles in the emulsion of WBC at first, and then, those particles fused,
flattened, and gathered together to form a continuous phase by precipitation during the baking stage. Further, an acrylic polymer layer was found to exist on the substrate.

Such a structure, acrylic polymer dispersed epoxy/phenolic polymer, gives the polymer chemical and physical characteristics inherent of the epoxy/phenolic polymers. Thus, the tough and chemically resistant characteristics of the epoxy/phenolic polymers are maintained and the cured film shows excellent hot water resistance. Although the epoxy/phenolic polymers are not in direct contact with the substrate and the mechanism of adhesion to the substrate differs from that for solvent borne coatings, excellent adhesion to the substrate is also developed.

Nomenclature

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBC</td>
<td>Waterborne coatings</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>IR spectroscopy</td>
<td>Infrared spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TFS</td>
<td>Tin free steel</td>
</tr>
<tr>
<td>E'</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>E''</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>tan δ</td>
<td>Loss tangent</td>
</tr>
<tr>
<td>T_g</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
</tbody>
</table>

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References


CHAPTER 5. OBSERVATION OF LEVELING PROCESS

5-1. Introduction

As discussed in Chapter 1, it is quite important to obtain a flat smooth coated surface as to develop the inherent performances of the coating films in industrial coatings. It is also necessary to improve the application characteristics including leveling during the process for commercial application of the waterborne coatings, WBCs.[1-5] Thus, a systematic study has been carried out to understand the mechanism of leveling flow and to obtain WBCs with improved leveling properties.

In this chapter, an observation method of leveling process is described and the results obtained are compared with the previous results[6]. The observed results were also compared with the results predicted by the previous theories[6-10].

5-2. Observation System

5-2-1. Film application

It is essential to employ a method for the reproducible application of a thin film having a wavy surface on a flat substrate for the experimental study of the kinetics of leveling of a wavy fluid surface. Following Overdiep[4], the fluid film was applied by means of a doctor blade with the knife edge cut to a block shape, as shown in Fig. 5-1.

The cross section of the film ripples is thought initially to have the same block-shaped profile, which can be described by the following Fourier series:
Fig. 5-1 The knife edge of the doctor blade employed (not in scale)

\[ z = \sum b_m \sin(\frac{2m\pi}{\lambda} \cdot (x\cos\theta + y\sin\theta)) \]  

(5-1)

where \( a_m = a_0/m, \ \lambda_m = \lambda_0/m \) and \( \theta \) is the angle between the \( x \) axis and the perpendicular direction to the lateral direction of the surface ripples; see Fig. 5-2. The measurement was carried out under a constant condition of \( 2a_0 = 100\mu m \) and the average thickness of wet film was \( 150\mu m \).

By this method, some surface disturbance is produced on the ground wave. However, as suggested by Orchard's equation, Eq.1-1, the amplitudes of such waves of shorter wave lengths decay most quickly. Consequently, it is satisfactory to consider the decay rate of the amplitude of the ground wave only.

5-2-2. Bases on designing the observation system

It is important to note that there exists a great anisotropy on the scale of the surface ripples, called ribs, between the length of the lateral direction and the height, which makes it
difficult to observe the amplitude of the surface ripples optically. The length of the lateral direction and also the perpendicular direction to the direction of the surface ripples is so great that it is easily observable with the naked eye, whereas the height of the ripples is in the order of $2a_0 = 100 \mu m$ or less. Still, the existence of the surface ripples causes an inferior appearance. The observation system has to be constructed to follow the decay of the surface ripple amplitude.

Such a system was first proposed by Camina and Howell$^{(10)}$ and then modified by Overdiep$^{(1)}$. However, their systems were too complicated to reconstruct. Thus, a new observation system is composed here based on a modification of the above mentioned systems.
5-2-3. A common expression of the reflection of a slit-beam

Suppose that a slit-beam \( \mathbf{a} \), which is parallel to the \( x \) axis, is injected to the observation plane with a normal vector \( \mathbf{n} \) at an incident angle \( \alpha \) to the \( z \) axis and the slit-beam is reflected on the plane to the direction \( \mathbf{b} \), see Figs. 5-2 and 5-3. Then, the relationships can be expressed as follows;

\[
\mathbf{n} = [\sin \phi \cos \theta, \sin \phi \sin \theta, \cos \phi] \quad (|\mathbf{n}| = 1) \tag{5-2}
\]

\[
\mathbf{a} = [0, \sin \alpha, -\cos \alpha] \quad (|\mathbf{a}| = 1) \tag{5-3}
\]

\[
\mathbf{b} = -2(\mathbf{n} \cdot \mathbf{a}) \mathbf{n} + \mathbf{a} \quad (|\mathbf{b}| = 1) \tag{5-4}
\]

The slit-beam reflected from a smooth observation plane is projected on a screen that is placed normal to the reflection direction \( \mathbf{b}_p \) at a distance \( H_p \) from the reflection point. The coordinate vectors \( \mathbf{x}_p \) and \( \mathbf{y}_p \) on the projection plane are defined as \( \mathbf{x}_p \) to be parallel to the slit-beam, as follows.

\[
\mathbf{b}_p = [0, \sin \alpha, \cos \alpha] \quad (|\mathbf{b}_p| = 1) \tag{5-5}
\]

\[
\mathbf{x}_p = [1, 0, 0] \quad (|\mathbf{x}_p| = 1) \tag{5-6}
\]

\[
\mathbf{y}_p = [0, -\cos \alpha, \sin \alpha] \quad (|\mathbf{y}_p| = 1) \tag{5-7}
\]

The reflected slit-beam is projected on this plane, and the length \( H \) is defined to be the distance between the observation plane and the projection plane along the vector \( \mathbf{b} \).

\[
H \mathbf{b} = H_p \mathbf{b}_p + u \mathbf{x}_p + v \mathbf{y}_p \tag{5-8}
\]
Thus, we obtain the following relationship, see Fig. 5-3.

\[ H_p = H (b \cdot b_p) \]  

(5-9)

\[ u = H (b \cdot x_p) = H_p \frac{(b \cdot x_p)}{(b \cdot b_p)} \]  

(5-10)

\[ v = H (b \cdot y_p) = H_p \frac{(b \cdot y_p)}{(b \cdot b_p)} \]  

(5-11)

5-2-4. Determination of the ripple amplitude from the strain of the projected slit-beam

Suppose that there are ripples on the observation plane, and that the angle between the perpendicular direction to the lateral direction of the ripples and the \( x \) axis is defined to be \( \theta_r \). Then the surface irregularity can be expressed by the Fourier series expressed by Eq. 5-1.

The slope at a point on the plane is expressed as follows;

\[
\frac{\partial z}{\partial x} = \sum_m b_m \frac{2m\pi}{\lambda} \cos(\frac{2m\pi}{\lambda} (x \cos \theta_r + y \sin \theta_r)) \cdot \cos \theta_r
\]

\[
= \sum_m A_m \cos B_m t \cdot \cos \theta_r
\]  

(5-12)

\[
\frac{\partial z}{\partial y} = \sum_m b_m \frac{2m\pi}{\lambda} \cos(\frac{2m\pi}{\lambda} (x \cos \theta_r + y \sin \theta_r)) \cdot \sin \theta_r
\]

\[
= \sum_m A_m \cos B_m t \cdot \sin \theta_r
\]  

(5-13)

where:
Thus, the normal vector at the point of observation on the ripple surface can be determined as follows:

\[ \mathbf{n}_r = \left[ \frac{-\Sigma A_m \cos B_m t \cdot \cos \theta_r}{\sqrt{1 + (\Sigma A_m \cos B_m t)^2}}, \frac{\Sigma A_m \cos B_m t \cdot \sin \theta_r}{\sqrt{1 + (\Sigma A_m \cos B_m t)^2}} \right] \frac{1}{\sqrt{1 + (\Sigma A_m \cos B_m t)^2}} \]  

(5-15)

The coordinate point \((u, v)\) on the projection plane, which corresponds to the coordinate point \((x, y)\) on the observation plane, is obtained as follows, using Eqs. 5-8, 5-9 and 5-10:

\[ (u, v) = (x + H_p \left( \frac{\mathbf{b}_r \cdot \mathbf{x}_p}{\mathbf{b}_r \cdot \mathbf{b}_p} \right), H_p \left( \frac{\mathbf{b}_r \cdot \mathbf{y}_p}{\mathbf{b}_r \cdot \mathbf{b}_p} \right) \]  

(5-16)

where it is set to be \(y=0\) at the point of observation.

The amplitude of the surface ripples of the coated wet film is far smaller than the wave length, and the shape of the surface ripples is observed to possess a gentle, sinusoidal nature. Thus, it is reasonable to assume as follows:

\[ b_m \ll \lambda / 2 \pi m \]  

(5-17)

By comparison of Eq. 5-2 with Eq. 5-15, we obtain the following equations.

\[ \sin \phi = -\frac{\Sigma A_m \cos B_m t}{\sqrt{1 + (\Sigma A_m \cos B_m t)^2}} \approx -A_1 \cos B_1 t \]  

(5-18)
\[
\cos \phi = \frac{1}{\sqrt{1 + (\sum A_m \cos B_m t)^2}} - 1
\]  

(5-19)

And, from Eqs. 5-16, 5-18 and 5-19, we obtain:

\[
u = x + 2H_p \cos \theta \cos \alpha \sum A_m \cos B_m t
\]

(5-20)

\[
v = -2H_p \sin \theta \sum A_m \cos B_m t
\]

(5-21)

So far we have discussed the influence of the slope of the ripples on the observation plane on the slit pattern on the projection plane. Next, we will consider the influence of the height of the ripples on the slit pattern on the projection plane.

Assume that the surface ripples have no slope and have stepwise gaps with height, \( h_r \). The dislocation of the slit pattern on the projection plane, \( d \), is expressed as follows, see Figs. 5-2 and 5-3;

\[
d = 2h_r \sin \alpha
\]  

(5-22)

which is negligible when \( h_r \ll H_p \).

To record the slit pattern on the projection plane using a camera with magnification rate \( H_c \), the coordinate point of the pattern on the camera plane is defined as \( (u_c, v_c) \), which can be derived using Eqs. 5-20 and 5-21.
As mentioned above, it is possible to observe the slit pattern distorted by the slope of the surface ripples by this optical system. Further, it is possible to determine the amplitude and the wave length of the surface ripples directly from the slit pattern, because the surface ripples are assumed to be sinusoidal shape in nature. This is expressed as follows, using Eqs. 5-14, 5-23 and 5-24:

$$\lambda = \frac{2 \cos \theta_i}{H_c} \cdot \Delta u_c$$  \hspace{1cm} (5-25)
\[
\alpha_1 = -\frac{\lambda}{4\pi} \cdot \frac{1}{H_c H_p} \cdot \frac{V_{c,\text{max}}}{\sin\theta_r} = -\frac{\cot\theta_r}{2\pi H_c^2 H_p} \cdot \Delta u_c \cdot V_{c,\text{max}} 
\]  

(5-26)

where, \(\Delta u_c\) is defined as the distance between the neighboring \(u_c\)s at \(V_c = 0\).

5-2-5. The optical system and the analysis of the results

An optical system was constructed to measure the decay of the amplitude of the surface ripples on a coated wet film, which is schematically shown in Fig. 5-4. The measurements were carried out at a constant condition of \(\alpha = 45^\circ\) and \(\theta_r = 45^\circ\).

A He-Ne laser (633nm, 0.8mW) was used as the light source, and the laser beam was changed to a slit-beam using cylindrical lenses. It is preferable to use a slit beam with a higher degree of parallel to obtain higher accuracy, owing to the narrowing of the width of the line of the projected pattern on the projection plane. It was possible to obtain a parallel light with the diffusion angle of 2' for the lateral direction and 0'12" for the vertical direction, which is thought to be sufficiently small.

The projected image was recorded by a high speed video camera with a close-up lens, MICRO NIKKOR 105 mm, at a rate of 400 images per second. Some of the recorded images were printed out using a video copy processor to determine \(V_{c,\text{max}}\) and \(\Delta u_c\); see Fig. 5-5. The system was calibrated by placing a transparent scale on the focus plane of the close-up lens to determine the position of the projection plane, which gives the value of \(H_p\). Furthermore, from the printed image of the
Fig. 5-4 Arrangement of the optical system

Fig. 5-5 Projected image recorded by a video camera; top: 10.0 seconds, center: 15.0 seconds, and bottom: 20.0 seconds after application
5-3. Observation of Leveling Process

*Figure 5-6* shows the observation results of the leveling process for a waterborne coating, WBC, with no co-solvents, one with 5% ethylene glycol *mono*-hexyl ether, EGHE, one with 5% *n*-butyl alcohol, *n*-BuOH, and for a solvent-borne counterpart. In the case of the WBC that contains *n*-BuOH, the surface waviness disappeared at once and then it re-appeared. From careful inspection of the photographs of the images of the reflected light beam, the crests of the ripples were formed where the troughs of the original surface ripples were located and vice versa, as observed by Overdiep\(^6\) for a solvent-based alkyd paint. Thus, it seems reasonable to give negative values for the amplitudes of the re-appeared surface ripples. As *Fig. 5-6* shows, the leveling of thermosetting WBCs proceeded very quickly, even faster than the conventional solvent-borne counterpart when the proper co-solvent is employed and the leveling was complete within 20 s and did not proceed any further. It also shows that the effects of a co-solvent are pronounced on the leveling phenomenon.

The negative amplitude or the re-appearance of the surface ripples was observed for a WBC that contains *n*-BuOH and the solvent-borne counterpart. However, for the two WBCs, one with no co-solvent and one with EGHE, the negative amplitude was not observed. Thus, the occurrence of the negative amplitude of the surface ripples is considered to be closely related to the solvent composition or the co-solvent added.
Fig. 5-6 The relationship between the amplitude of a surface wave and time. Marks denote; a WBC with 5% of n-BuOH (▲), with 5% of EGHE (○), with no co-solvent (●) and a solvent borne counterpart (△).

5-4. Comparison with the Previous Theories

5-4-1. Orchard's theory\textsuperscript{(8,9)}

The data presented in Fig. 5-6 were replotted in Fig. 5-7 to show the time dependence of the logarithm of the absolute value of \( a/a_0 \). The original theory predicts that \( \log(a/a_0) \) is proportional to time, \( t \), if the viscosity of the fluid is constant throughout the leveling process; see Eq. 1-1. The behavior of the solvent-borne coating appears to be consistent with the prediction. However, the behavior of the WBCs with or without co-solvents contradicts to the prediction.

The constant, \( C_1 \), in Eq. 1-1 can be subdivided as follows:\textsuperscript{(9)}:
Because the factor $16\pi^4h^3/3\eta\lambda^4$ does not depend on the characteristics of the coated fluid, it is possible to apply the following relation; although these coating materials do not show Newtonian characteristics, their power constants are very similar in magnitude and it is reasonable to assume that the rheological properties are similar:

$$C_1 \propto \gamma/\eta \approx C_4$$  \hspace{1cm} (5-28)

The values of the initial surface tension, $\gamma$, the initial viscosity of the fluid, $\eta$, and $C_4$ are listed in Table 5-1 with the relative magnitudes of $C_4$ divided by that of the WBC.
containing EGHE, $C_5 = C_4 / C_4^{EGHE}$. Using the reduced time, $t \cdot C_5$, it is predicted from the original theory that a consistent leveling rate can be obtained independent of the co-solvent added. However, as shown in Fig. 5-8, even the initial leveling rates were not coincident, where the magnitude of the re-appeared surface ripples are not plotted to compare the initial leveling rates.

Moreover, it is impossible to predict the re-appearance of the surface ripples from the original theory. Thus, it seems reasonable to conclude, as pointed out by Overdiep, that this

![Graph showing the relationship between log(a/a₀) and reduced time.](image)

Fig. 5-8 The relationship between the amplitude of a surface wave and the reduced time. Marks are the same as in Fig. 5-6
Table 5-1  The viscosity of the original fluid at 1 sec^{-1} (K/mPa-s), surface tension (γ/N-m^{-1}),
C_4 = γ/K and C_5 = C_4/C_4^{EGHE}.

Coating A : the WBC containing n-BuOH,
Coating B : the same containing EGHE,
Coating C : the same with no co-solvent,
Coating D : the solvent borne counterpart

<table>
<thead>
<tr>
<th>COATINGS</th>
<th>K</th>
<th>γ</th>
<th>C_4</th>
<th>C_5</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.57</td>
<td>34.7</td>
<td>22.1</td>
<td>1.87</td>
</tr>
<tr>
<td>B</td>
<td>2.84</td>
<td>33.5</td>
<td>11.8</td>
<td>1.00</td>
</tr>
<tr>
<td>C</td>
<td>0.83</td>
<td>40.4</td>
<td>48.7</td>
<td>4.12</td>
</tr>
<tr>
<td>D</td>
<td>1.88</td>
<td>27.6</td>
<td>14.7</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Theory fails to give even a qualitative description of the leveling process of the WBCs studied here.

The discrepancy mainly comes from the fact that the change of the surface tension, the viscosity of the fluid, and the development of surface tension gradient by the evaporation of the volatile components were not accounted for in the theory. Even if the integrated fluidity is accounted for, as discussed by Orchard[8,9], it seems impossible to describe the re-appearance of the surface ripples, because the theory assumes a homogeneous viscosity and surface tension throughout the coated film.

5-4-2. Camina's treatment[10]

The theory of Orchard was extended to apply to a power law fluid; see Eq. 1-2. The equation can be simplified as follows:

\[ \frac{da}{dt} = -C_6 \left( \frac{\gamma}{\eta_t} \right)^{1/N} \]  \hspace{1cm} (5-29)
and,

\[ \eta_t = \eta_i e^{rt} \]  \hspace{1cm} (5-30)

where \( \eta_t \) is the viscosity at time \( t \), \( \eta_i \) is the initial viscosity, \( r \) is a solvent parameter, \( C_6 \) is a constant. Because \( \eta_t \) is an increasing function of time \( t \), \( \frac{d\eta}{dt} \) decreases with \( t \). In other words, this means that the leveling rate decreases due to the viscosity build-up by the evaporation of volatile components during the leveling process. Thus, they proposed that Orchard's theory was extended to the non-Newtonian fluids and that it had become possible to predict the leveling ability of paints, particularly if solvent evaporation was taken into account. However, the effects to introduce the assumption of the power law fluid are not clearly reflected on the results. It is still impossible to predict the re-appearance, i.e., the negative amplitude, of the surface ripples and also the effects of co-solvents.

5-4-3. The theory of Overdiep\[^{[6,7]}\]

Overdiep derived an integro-differential equation to express the course of the wave amplitude decay, Eq. 1-3. Because the analytical solution of this equation is unknown, he tried to use a stepwise computational method. However, even if the quantities \( C_2 \), \( C_3 \), and \( \eta \) are determined experimentally, it is still difficult to draw the course of leveling using the equation. This diminishes the usefulness of the equation, although the effects caused by the evaporation of the solvent were taken into account. Moreover, when \( C_3 \neq 0 \), it is
possible to predict the occurrence of the negative amplitude in the course of leveling from Eq. 1-3. The constant $C_3$ can be calculated from the composition of the coating, the initial geometry of the coated film, the evaporation rate of the solvent, the surface tension of the coating and the rate of the surface tension increase by the solvent evaporation; and it is positive for most coating materials, including those studied here. The integration in Eq. 1-3 gives a positive value for $a$, and so $da/dt$ is a constantly decreasing function as long as $a$ is positive. When $a$ decreases to be less than zero, then it becomes possible to give a positive value of $da/dt$, which may correspond to the leveling of the re-appeared surface ripples. Even though the equation seems reasonably qualitative, it is still impossible to predict the occurrence or the non-occurrence of the negative amplitudes of the surface ripples. As presented here and elsewhere, the re-appeared surface ripples could be observed for some coating materials with volatile components, but not for all of them.

However, the concept of the surface tension gradient proposed by Overdiep as a driving force to promote leveling seems important. We experimentally found that it is preferable to add a co-solvent that evaporates faster and lowers the surface tension of the WBCs, as discussed in the following section. The surface tension of the WBC with no co-solvent is in the range of 40 mN·m$^{-1}$, which can be lowered to about 35 mN·m$^{-1}$ by the addition of a co-solvent; see Table 5-1. The addition of a co-solvent with a higher vapor pressure was also found effective in improving the leveling performance of
WBCs. However, it should be noted that the addition of a solvent with too high a volatility should be avoided because it might evaporate prior to application on the substrate.

This fact can be explained by means of the surface tension gradient. It will be reasonably assumed that the amount of evaporated materials from a unit surface area of the coated film under a given condition is equivalent at the crest portion and at the trough portion of the surface ripples. If the solvent added evaporates faster than water, then the average concentration of the solvent at the crest portion is higher than that at the trough portion. This results in the development of surface tension gradients to promote the flow of the coated fluid from the crest to the trough. The higher the efficiency of the solvent to lower the surface tension of the WBCs is, and the higher the volatility of the solvent is, the sharper the surface tension gradients will be formed, which will help to accelerate leveling.

As discussed so far, the original theory is important to understand the course of leveling; and the development of the surface tension gradients has been taken into account. However, it is insufficient to predict the leveling performance of a given coating material. Overdiep introduced the concept of total flow to take the effects of the evaporation of the solvent into account; however, it seems insufficient to describe the effects of the solvent evaporation, namely the increase in the viscosity and the surface tension, the development of the surface tension gradient, and so on, by this single factor. Thus, a systematic study has been undertaken in our laboratory
to understand the leveling process, and the results will be discussed in the following chapters. It seems to be essential to avoid the assumption of creeping flow, i.e., the negligible inertial force. The re-appearance of the surface ripples cannot be explained without the effects of inertia, which will be also discussed in the following chapters.

5-5. The Surface Texture of the Cured Film

WBCs with a variety of co-solvents were coated on tin free steel, TFS, sheets with a forward roll coater and the coated TFS sheets were baked at 210°C for 10 min in a gas forced air oven. The coated surface was then analyzed by a needle scan type surface texture measuring instrument, Surfcom, produced by Toyo Seimitsu Co., Ltd., Tokyo, to determine the final surface waviness.

Figure 5-9 shows the results. As the Figure shows, the surface smoothness was improved by the addition of a co-solvent and the surface smoothness depended on the co-solvent added, although the best leveling appears to have been obtained with a WBC with no co-solvent from the leveling experiment; see Fig. 5-6. Smoothness comparable to the solvent borne counterpart is obtainable by careful selection of a co-solvent. The surface smoothness does not correlate with the observation results of the leveling process; neither the initial leveling rate nor the ultimate amplitude of the ripples.

It appeared as if the leveling process did not proceed any further after 20 s. However, the viscosity of the coated film was confirmed to be still low enough to flow, from the fact that
the formation of craters was observed 100 s after the application of the coatings. If the viscosity of the coated film is sufficiently low to form craters after the end of the leveling process, it seems still possible to flow, although the drastic decrease in the leveling rate appears to be the end of the leveling process.

Thus, it is reasonable to assume that the leveling rate increases again with the elevation of temperature when the coated sheets are baked in an oven. It seems likely that a coated film with more residual solvent will flow more easily to give a smooth surface, even if its leveling rate at the initial stage
is low, as in the case of the solvent-borne counterpart, which is thought to be the reason for the discrepancy of the observed leveling process and the smoothness of the ultimately obtained baked film.

5-6. Concluding Remarks

A modified observation system for the leveling process of thermosetting waterborne coatings was proposed. It has become possible to observe the course of the wave amplitude decay after application, and the results obtained were consistent with those reported previously.

A great discrepancy was found between the previously proposed theories on the leveling of coated fluids and the observation results, as pointed out by Overdiep[6]. Effects arising from the evaporation of the solvent were not taken into account in the original theory of Orchard, et al.[6,9], and the theories based on it, which made the theory not applicable for coating materials containing volatile components.

The theory of Overdiep[6] seems reasonable. However, it is insufficient to describe the leveling behavior of the thermosetting waterborne coatings studied here. It was impossible to predict the course of wave amplitude decay without leveling experiments by the theory and to distinguish the coatings with and without the negative wave amplitude, which diminishes the usefulness of the theory. However, the qualitative consistency in the occurrence of the negative wave amplitude encourages us to widen the understandings of the leveling process of thermosetting waterborne coatings.
Nomenclature

\( WBC \) : Waterborne coating

\( a_0 \) : The initial amplitude of ripples

\( a \) : The amplitude of ripples at time \( t \) after application

\( C_1 \) : A constant

\( \eta \) : Viscosity of the coated fluid

\( N \) : The power constant

\( K \) : The viscosity at 1 sec.\(^{-1} \)

\( \gamma \) : The surface tension of the coated fluid

\( \lambda \) : The wavelength of the ripples

\( \pi \) : The ratio of circumference

\( h \) : The mean film thickness

\( C_2, C_3 \) : Constants

\( b \) : Constants

\( \theta_r \) : The angle between the perpendicular direction to the lateral direction of the ripples and the \( x \) axis

\( \phi \) : The angle between the normal vector of the observation plane and the \( x \) axis

\( \theta \) : The angle between the normal vector of the observation plane and the \( z \) axis

\( \alpha \) : The incident angle of the slit-beam to the \( z \) axis

\( n \) : The normal vector at a point of interest on the observation plane

\( a \) : The vector of the injected slit-beam

\( b \) : The vector of the reflected slit-beam
\( \mathbf{b}_p \) : The vector of the reflected slit-beam from the horizontally placed observation plane

\( H_p \) : The distance between the projection plane and a point of interest along the vector \( \mathbf{b}_p \)

\( \mathbf{x}_p, \mathbf{y}_p \) : The coordinate vectors on the projection plane

\( H \) : The distance between the observation plane and the projection plane along the vector \( \mathbf{b} \)

\( \mathbf{n}_r \) : The normal vector at a point of interest on a ripple

\( A_m, B_m \) : Constants

\((u, v)\) : The coordinate point on the projection plane which corresponds to \((x, y)\) on the observation plane

\( \mathbf{b}_t \) : The vector of the reflected slit-beam from a ripple

\( h_t \) : The height of the stepwise gaps on the coated surface

\( d \) : The dislocation of the slit pattern on the projection plane

\((u_c, v_c)\) : The coordinate point on the camera plane which corresponds to \((u, v)\)

\( \Delta u_c \) : The distance between the neighboring \( u_c \)s at \( v_c = 0 \)

\( H_c \) : The magnification rate of the camera

\( v_c, \text{max} \) : The maximum amplitude of \( v_c \)

\( \text{EGHE} \) : Ethylene glycol mono-hexyl ether

\( C_4 \) : \( C_4 = \gamma / \eta \)

\( C_5 \) : \( C_5 = C_4 / C_4^{\text{EGHE}} \)

\( C_4^{\text{EGHE}} \) : \( C_4 \) for the waterborne coating containing EGHE
\[ C_6 : \quad C_6 = \frac{-N}{2N+1} \left( \frac{2\pi}{\lambda} \right)^{3N} \cdot h^{2N+1} \]

\[ \eta_t : \quad \text{The viscosity of the coated fluid at time } t \text{ after application} \]

\[ \eta_i : \quad \text{The initial viscosity of the coated fluid} \]

\[ r : \quad \text{A solvent parameter} \]

References

6-1. Introduction

In the previous chapter, we showed that the leveling process of coatings containing volatile components is quite different from that of coatings without any volatile components. This means that the changes in the composition of coated wet films by evaporation of volatile components show a significant influence on the leveling process of coated films. Those changes in the composition may result in the changes in the viscosity and in the surface tension and produce a viscosity gradient and a surface tension gradient depending on the variation of film thickness, which are assumed to accelerate or decelerate leveling. Thus, it is essential to know the drying process to discuss the leveling of coated wet films containing volatile components.

In this chapter, the drying process of thermosetting waterborne coatings, WBCs, is discussed including the change of concentrations of water and the co-solvents in the coated wet films, the viscosity and the surface tension, which will be used to discuss the leveling process in the following chapters.

The drying process of paint films has been extensively studied. The universal functional activity coefficient, UNIFAC, method was established to estimate the volatilities of the solvents and solvent mixtures. The evaporation behavior from WBCs were also studied. The findings are helpful in understanding the drying behavior of the thermosetting WBCs discussed here. However, most of the studies were designed to understand the complete process of drying, i.e., time
required to achieve a tack-free state for air-drying coatings. In the case of thermosetting WBCs discussed here, the leveling is complete within a short time, within 20 seconds, after only a small amount of solvent evaporation\textsuperscript{[11]}. Thus, it is important to understand the initial stage of the drying process accurately, and to analyze the changes in viscosity and surface tension of the wet films by changes in the composition. It is also important to estimate the extent of the surface tension gradient development in the wet films by partial drying\textsuperscript{[1,19]}.

The drying of waterborne paints proceeds in two stages, an initial stage with a fast and constant evaporation rate and a second stage of slow diffusion-controlled evaporation\textsuperscript{[11]}. The initial stage continues for at least 200 seconds\textsuperscript{[13,18]}. Because the leveling is complete within a short period of time, it is satisfactory to consider the initial stage of drying only to discuss leveling. However, it is difficult to follow the evaporation which occurs in such a short time. Thus, the evaporation behavior was predicted by a computer simulation technique using the Shell Solvent Blend Evaporation Program developed by Shell Development Company\textsuperscript{[17]}.

6-2. Definition of Total Evaporation

We define total evaporation, $\alpha(t)$, as the ratio of the total amount of evaporated materials up to time $t$, $E(t)$, based on the initial amount of the volatile components, $E_0$, assuming that the density of the aqueous phase is unity, as follows;

$$\alpha(t) = \frac{E(t)}{E_0}$$  \hspace{1cm} (6-1)
$E(t)$ and $E_0$ are given as follows;

$$E(t) = v_o \cdot t \quad (6-2)$$

$$E_0 = \langle h_0 \rangle \cdot (1-n_0) \quad (6-3)$$

where, $v_0$ is the initial evaporation rate characteristic to the specific WBC, $\langle h_0 \rangle$ is the initial film thickness, and $n_0$ is the initial concentration of non-volatiles in the WBC. The calculated composition of the evaporated materials was directly applied to the evaporation from WBCs, assuming that the effects of resins can be neglected. The assumption was experimentally verified for the case of a WBC containing iso-butanol, WBC/i-BuOH.

Knowing that the composition of volatile components remained in the wet films at a given time after application, WBCs with given compositions were prepared and their rheology and surface tensions were analyzed.

6-3. Evaporation Behavior of Water/Solvent Mixture

The evaporation behavior of mixed solvent, water/i-BuOH, blend was predicted using the Shell Solvent Blend Evaporation Program (AQUEVAP) developed by Shell Development Company. Calculations were carried out with Dr. V. Higgins for given compositions and evaporation conditions.

In the evaporation of solvent mixtures, the interactions between the components play an important role. External conditions such as temperature and pressure have to be accounted for. The relative humidity, RH, also influences the
evaporation rate of water/solvent mixture.

To predict this phenomenon, the UNIFAC method has been established and the Shell Solvent Blend Evaporation Program was developed by Shell Development Company\textsuperscript{[17]}. It is possible to calculate: (1) the time required to evaporate 5% aliquot, and (2) the composition of residual mixed solvent at 2% aliquot, for a given composition of solvent mixture at 25°C at a given relative humidity. However, it is impossible to calculate the evaporation behavior of an immiscible blend by the computer program, even though a variety of water-immiscible solvents are miscible with a WBC.

Water-immiscible solvents can be used as co-solvents of WBCs. Most of these water-immiscible co-solvents are assumed to exist in the dispersed particles with the epoxy/phenolic resin in the WBCs. These water-immiscible solvents are thought to be dissolved in the aqueous medium of the WBCs only up to their saturation concentration. By contrast, water-miscible solvents are thought to exist both in the aqueous phase and in the resin particles, and their concentration in the aqueous phase is much higher than that of water-immiscible solvents.

Figures 6-1 and 6-2 show examples of calculated evaporation behavior for a mixture of water/$i$-BuOH = 65/5 at 25°C under several relative humidities. The evaporation rate was strongly affected by the relative humidity, see Fig. 6-1. As noted, it is important to know accurately the behavior of the initial portion of the process to discuss the leveling of the wet films. The slopes of the curves give the evaporation rate, and the initial evaporation rate is given in Table 6-1 with their
Fig. 6-1  Evaporation behavior of H₂O/i-BuOH=65/5 blend at 25°C. Marks denote: △: at 0% RH, ○: at 25% RH, ●: at 50% RH and ▲: at 65% RH

Fig. 6-2  i-BuOH content in the residue during evaporation of H₂O/i-BuOH=65/5 blend at 25°C. Marks are the same as in Fig. 6-1.
Table 6-1  The calculated initial evaporation rate of water and water/i-BuOH=65/5 blend at varying relative humidity.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Water</th>
<th>Water/i-BuOH=65/5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial Evaporation Rate (%/s)</td>
<td>Relative Intensity ( I_r )</td>
</tr>
<tr>
<td>0</td>
<td>6.67x10^{-2}</td>
<td>2.00</td>
</tr>
<tr>
<td>25</td>
<td>5.00x10^{-2}</td>
<td>1.50</td>
</tr>
<tr>
<td>50</td>
<td>3.33x10^{-2}</td>
<td>1.00</td>
</tr>
<tr>
<td>65</td>
<td>2.33x10^{-2}</td>
<td>0.70</td>
</tr>
</tbody>
</table>

relative intensity, \( I_r \), based on one for water and one for a water/i-BuOH=65/5 blend at 50% RH. Thus, the evaporation rate of a WBC at various relative humidities can be estimated using the experimentally determined evaporation rates at 50% RH.

From the data in Fig. 6-2, it is possible to calculate the amount of evaporated water and i-BuOH. Figure 6-3 shows the calculated results at 50% RH. The evaporation rate of water is affected by the atmospheric relative humidity, but the evaporation rate of solvents is not. In other words, the differences in the evaporation rate because of the atmospheric relative humidity is totally dependent on the evaporation rate of the water.

6-4. Evaporation Behavior from Waterborne Coatings

The emulsion was diluted by deionized water and/or a co-solvent to give 30% NV after stripping solvents. This emulsion was used to measure the volatilities of water and a co-solvent. A variety of co-solvents were evaluated. The evaporation behavior of a WBC was monitored at 25°C, 50% RH and
Fig. 6-3 Composition of evaporated components during evaporation of \( H_2O/i\text{-BuOH}=65/5 \) blend at 25\(^\circ\)C at 50\% RH

with negligible air flow, i.e., in a closed chemical balance.

First, the weight of an empty aluminum laboratory dish with 11.3 cm\(^2\) open surface was measured \( W_1 \). Then, about 3 grams of the WBC sample was poured into the laboratory dish and the weight was monitored at time intervals of 30 seconds for up to 10 minutes. After monitoring the weight change, the laboratory dish was heated on a hot plate to slowly dry the WBC, and then the coating was baked at 200\(^\circ\)C for 10 minutes in an oven. After cooling, the weight was measured \( W_2 \). The difference, \( W_2 - W_1 \), gives the total amount of NV used. For this, we determined the exact amount of sample used, \( (W_2 - W_1)/0.30 \), because the initial sample was \( n_0 = 0.30 \), i.e., 30\% NV. The evaporation data was
extrapolated to determine the exact starting time, i.e., \( t=0 \).

*Figure 6-4* shows an example of evaporation behavior of a WBC containing \( i\)-BuOH. It is reasonable to determine the initial evaporation rate from the slope of the initial portion of the curve. *Table 6-2* shows the initial evaporation rates for WBCs containing a variety of co-solvents. By comparison of the data with one containing no co-solvent, WBC/\( H_2O \), the solvents are classified in three categories; ones which accelerate evaporation by stoichiometric evaporation, ones which do not affect the evaporation rate of the WBC/\( H_2O \), and ones which reduce the evaporation rate. It appears that only water evaporates from the WBCs which contain the solvent in the second category and that the solvent in the third category reduces the volatility of

*Fig. 6-4* Evaporation behavior of the WBC/\( i\)-BuOH
water from the WBCs. The analysis of wet films by a gas chromatograph showed that the amount of evaporated solvent was negligible for the solvents in the last two categories. Thus, it is reasonable to assume that no solvent evaporates from the wet film of a WBC which contains the solvent in the last two categories.

6-5. Drying of the Coated Wet Films

From the data in Table 6-2, it is possible to calculate the amount of retained volatile components in the wet film of a WBC at various film thicknesses. Figure 6-5 shows the calculated results for the WBC/H₂O. The water, H₂O, content is based on the composition prior to application, i.e., 70%.

For a WBC containing a solvent in the second and third categories, the evaporated amount of water is easily calculated

Table 6-2  Initial evaporation rate of WBCs containing various solvents at a 5% concentration determined experimentally at the condition of 25°C, 50% RH.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Initial Evaporation Rate (μg·cm⁻²·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>3.33</td>
</tr>
<tr>
<td>Methyl Alcohol</td>
<td>4.44</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>3.56</td>
</tr>
<tr>
<td>n-Propyl Alcohol</td>
<td>4.00</td>
</tr>
<tr>
<td>n-Butyl Alcohol</td>
<td>3.67</td>
</tr>
<tr>
<td>i-Butyl Alcohol</td>
<td>3.67</td>
</tr>
<tr>
<td>n-Amyl Alcohol</td>
<td>3.33</td>
</tr>
<tr>
<td>n-Hexyl Alcohol</td>
<td>3.22</td>
</tr>
<tr>
<td>Ethylene Glycol mono-Butyl Ether</td>
<td>3.22</td>
</tr>
<tr>
<td>Ethylene Glycol mono-Hexyl Ether</td>
<td>3.33</td>
</tr>
<tr>
<td>Butyl Carbitol</td>
<td>3.11</td>
</tr>
<tr>
<td>Methyl i-Butyl Ketone</td>
<td>4.89</td>
</tr>
</tbody>
</table>
because the evaporation of the solvent is negligible. However, it is more complicated to calculate the amount of retained water and solvent for a WBC which contains a solvent in the first category. Assuming that the existence of resins does not affect the volatility of the water/solvent mixture, it is possible to calculate the ratio of the evaporated water and solvent using the estimated solvent blend evaporation rates. First, the total amount of evaporation was calculated using the data in Table 6-2, and the results were interpolated in the data of Fig. 6-3. Interpolation was carried out by linear approximation. The interpolated results appeared to possess reasonable accuracy, and now it has become possible to separate

Fig. 6-5 Water content in the coated wet film of the WBC/H₂O with various initial film thicknesses during drying at 25°C, 50% RH.
Fig. 6-6 Calculated i-BuOH content in the coated wet film of the WBC/i-BuOH with various initial film thicknesses during drying at 25°C, 50% RH (○) and experimentally determined values for 100 μm thick film (●).

H₂O and i-BuOH. The calculated results of retained i-BuOH are shown in Fig. 6-6 for four initial film thicknesses.

To compare the calculated evaporation behavior with the experimental data, the solvent composition in the wet film containing i-BuOH was monitored. First, the WBC was coated on a tin free steel, TFS, sheet by a #60 coating bar to give an average film thickness of 100 μm. The coated TFS sheet was placed on a desk in a room controlled at 25°C, 50% RH, and negligible air flow. After 30 seconds, part of the wet film was picked up using a knife blade and placed in a sealed glass bottle for future characterization. The sample was analyzed by a gas chromatograph to determine the concentration of i-BuOH.
in the WBC, with added cyclo-hexanon as an internal standard. After the analysis, the bottle was opened and heated in an oven at 200°C for 10 minutes to determine the amount of NV. Total evaporation during the drying process was analyzed from these data and also estimated using the volatility data.

The experimentally determined values of retained i-BuOH for the wet film with an initial thickness of 100 μm are also shown in Fig. 6-6 for several values of decay time. The experimentally determined values were in good agreement with the calculated results, and verify that the effects of the resin component on the evaporation behavior were negligible.

6-6. Viscosity of the Coated Wet Films during Drying

Using the calculated evaporation data, WBCs were formulated to correspond to a total evaporation of 0, 0.030, 0.060, 0.090 and 0.120, respectively, based on the volatile components in the initial sample. A Haake viscometer RV 12 with a NV sensor was used. The viscosity measurement was carried out by up mode, gradually increasing the rotation speed up to the preset maximum value, at 25°C.

The WBCs during drying are assumed to be power law fluids expressed by the following equation;

\[ S = K \cdot D^N \quad (6-4) \]

where, S is the shear stress, K is a constant, D is the shear rate, and N is a power constant.

The power constant N was obtained from the data in the
higher shear rate region as a slope of the doubly logarithmic plot of shear stress vs. shear rate using the least square method. On the other hand, the constant K, which corresponds to the viscosity at 1 s⁻¹, was determined by extrapolating the data in the low shear rate region.

\[
f'(1 \text{ s}^{-1})
\]

\[
\eta = k \cdot \dot{\gamma}^{\frac{n}{2}}
\]

\[
\text{Total Evaporation}
\]

\[
\begin{array}{cccc}
0.12 & 0.09 & 0.06 & 0.03 & 0
\end{array}
\]

![Graph](image)

**Fig. 6-7** Rheological properties during drying of the WBC/i-BuOH.

Figure 6-7 shows the flow curves of WBC/H₂O at various levels of total evaporation. It demonstrates that the viscosity of a WBC increases with total evaporation; i.e. during the process of drying. The viscosities at 1 s⁻¹, K, are plotted in Fig. 6-8 with those of WBC/i-BuOH and the WBC with 5% ethylene glycol mono-hexyl ether, EGHE, WBC/EGHE. Table 6-3 shows the power constants, N. The viscosity of the WBC/EGHE
was higher than that of WBC/H₂O and the viscosity of the WBC/i-BuOH was lower. The Table also shows that the power constants are in a similar magnitude, i.e., 0.9. K was a linear function of the total evaporation, see Fig. 6-8, and it would be reasonable to apply the least square method to avoid experimental errors.

Table 6-3 The power constant of WBCs during drying.

<table>
<thead>
<tr>
<th>Total Evaporation</th>
<th>WBC/H₂O</th>
<th>WBC/i-BuOH</th>
<th>WBC/EGHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.97</td>
<td>0.89</td>
<td>0.90</td>
</tr>
<tr>
<td>0.03</td>
<td>0.96</td>
<td>0.87</td>
<td>0.84</td>
</tr>
<tr>
<td>0.06</td>
<td>0.91</td>
<td>0.87</td>
<td>0.89</td>
</tr>
<tr>
<td>0.09</td>
<td>0.89</td>
<td>0.90</td>
<td>0.88</td>
</tr>
<tr>
<td>0.12</td>
<td>0.84</td>
<td>0.96</td>
<td>0.91</td>
</tr>
</tbody>
</table>

The empirical relation is expressed as follows:

\[ K(t) = A \cdot \alpha(t) + B \]  

(6-5)

where, A and B are the constants and are listed in Table 6-4.

It is important to understand why the viscosity increases by the addition of EGHE and why the viscosity decreases by the addition of i-BuOH. The increase in size of dispersed particle by swelling is a possible factor to increase the viscosity of a WBC. Table 6-5 shows the changes in the mean particle size of the dispersed particles. The mean particle size increased slightly on the addition of a co-solvent, which could be one reason why the viscosity of a WBC was increased. Although the mean particle size of the dispersed particles
increased by the addition of a co-solvent, the distribution pattern of the particle size did not change much, which suggests that no new particles of emulsified solvent were formed. However, it is impossible to explain the viscosity decrease by the addition of i-BuOH from the data.

Fig. 6-8  Viscosity at 1 s⁻¹ for WBC/H₂O (○), WBC/i-BuOH (●) and WBC/EGHE (△).

Table 6-4  Experimentally determined constants of the empirical equation, Eq. 6-5.

<table>
<thead>
<tr>
<th>Constants</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBC/H₂O</td>
<td>7.60</td>
<td>0.456</td>
</tr>
<tr>
<td>WBC/i-BuOH</td>
<td>5.57</td>
<td>0.470</td>
</tr>
<tr>
<td>WBC/EGHE</td>
<td>11.2</td>
<td>0.602</td>
</tr>
</tbody>
</table>
Table 6-5 Mean particle size during drying of WBCs

<table>
<thead>
<tr>
<th>Total Evaporation</th>
<th>Mean particle size / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WBC/H₂O</td>
</tr>
<tr>
<td>0</td>
<td>0.66</td>
</tr>
<tr>
<td>0.03</td>
<td>0.67</td>
</tr>
<tr>
<td>0.06</td>
<td>0.67</td>
</tr>
<tr>
<td>0.09</td>
<td>0.67</td>
</tr>
<tr>
<td>0.12</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Another possible factor is the absorption of the co-solvent into the acrylic resin dissolved in the water. The neutralized acrylic resin may form a micell-like structure in water, based on the fact that the viscosity of an aqueous solution of the acrylic resin is lower than that of an organic solvent solution at the same concentration. If the co-solvent, EGHE, is absorbed into the micells and forms larger micells, but they are not larger enough to be detected by a particle size analyzer, the viscosity of the aqueous phase will increase. If the acrylic resin forms a relatively extended conformation by the absorption of the co-solvent, the result will be the same. These factors may explain the increase in the viscosity of a WBC with the addition of EGHE.

On the other hand, i-BuOH is completely miscible in water at this concentration, and the amount of absorption into the acrylic resin appears small. The micell size will be reduced by the existence of i-BuOH in water and the viscosity of water/i-BuOH blend will be lower than that of pure water, which can be why the viscosity of the WBC is reduced.

To obtain information on these points, some additional experiments were carried out. Aqueous solution of the acrylic
resin was prepared and diluted to the concentration corresponding to that in the WBCs during drying, with and without a co-solvent. The viscosity of these acrylic resin solutions was measured by a Brookfield viscometer. *Figure 6-9 shows the viscosities at 10 s⁻¹ during the drying process.* The viscosity of the aqueous solution of the acrylic resin with i-BuOH was much lower than that with no co-solvent. However, the viscosity of the aqueous solution of the acrylic resin with EGHE could not be determined because the solvent was immiscible in the aqueous phase and formed a separated layer. Thus, it will be reasonable to assume that the EGHE added is absorbed by the
acrylic resin to make the dispersed particles swollen and contributes to the increase in the viscosity of the WBC. The viscosity of the aqueous phase of the WBC is reduced by the addition of $i$-BuOH.

To discuss the leveling of wet films, knowledge of the rheological properties at the lower shear rate region is important. A Haake viscometer RV 20 with a ME45 sensor was utilized to evaluate the rheology of the WBCs in the lower shear rate region. **Figure 6-10** shows the shear rate dependence of the viscosity for the original WBCs, $\text{WBC}/H_2O$, $\text{WBC}/i$-BuOH and $\text{WBC}/\text{EGHE}$. The viscosities increase significantly with a decrease in the shear rate, and the assumption of a power law fluid is not valid in this shear rate region. However, the
shape of the viscosity vs. shear rate curves is suggested not to change much by evaporation, because the composition of WBC/\textit{i}-BuOH approaches that of WBC/H\textsubscript{2}O during the drying process.

6-7. Surface Tension of the Coated Wet Films during Drying

The surface tension was measured by the pendant drop method using \textit{System PD-Z} produced by Kyowa Kaimenkagaku Co., Ltd., Tokyo. The theoretical background of the analytical method has been given\textsuperscript{[10-11]}. The method has been claimed to be applicable to viscous liquids\textsuperscript{[12-14]}.

The surface tension of WBCs during evaporation was evaluated using the same sample as used for the viscosity measurements. Measurements were carried out at 25°C. The results are summarized in Fig. 6-11 as a function of the total evaporation. The surface tension, \( \gamma \), was a linear function of total evaporation expressed by the following equation;

\[
\gamma = C \cdot \alpha(t) + D
\]

(6-6)

where, \( C \) and \( D \) are the constant of the empirical equation.

\textit{Table 6-6} shows the results. The surface tension during drying is strongly affected by the co-solvent added; the addition of a co-solvent with high volatility increases the surface tension of a WBC during drying, whereas the addition of a co-solvent with lower volatility decreases the surface tension during drying. The addition of co-solvents is known to reduce the surface tension of WBCs. In the case of co-solvents with higher volatility such as \textit{i}-BuOH, the content of the co-solvent decreases during drying, which results in an increase in the
Fig. 6-11 Surface tension of WBC/H₂O (○), WBC/i-BuOH (●) and WBC/EGHE (△) during drying.

Table 6-6 Experimentally determined constants of the empirical equation, Eq. 6-6.

<table>
<thead>
<tr>
<th>Constants</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>WBC/H₂O</td>
<td>-13.3</td>
<td>46.3</td>
</tr>
<tr>
<td>WBC/i-BuOH</td>
<td>69.7</td>
<td>36.9</td>
</tr>
<tr>
<td>WBC/EGHE</td>
<td>-15.3</td>
<td>33.5</td>
</tr>
</tbody>
</table>

surface tension. By contrast, the surface tension of a WBC containing a lower volatility co-solvent such as EGHE decreases with the increase in the co-solvent concentration. In such cases, only water evaporates during the drying process. The surface tension of a WBC/H₂O decreases slightly during drying, perhaps by an increase in the resin concentration as suggested
by Overdiep\cite{19}. 

In the drying process, the concentration change of the volatile components by evaporation depends on the coated film thickness and the decay time after application, see Figs. 6-5 and 6-6. However, as noted, the concentration of the volatile components can be expressed as a function of the total evaporation, and the thinner the coated film, the faster the increase in the total evaporation. This suggests the development of the surface tension gradient dependent on the initial film thickness. Thus, in the case of the WBC/i-BuOH, the surface tension in the thicker portion tends to be lower than that in the thinner portion, which is thought to accelerate leveling. On the other hand, in the case of WBC/H$_2$O and WBC/EGHE, the surface tension gradient that developed is opposite to that of WBC/i-BuOH, which would decelerate leveling.

6-8. Concluding Remarks

It is important to understand the evaporation from a wet film to understand the leveling process of films. The evaporation of water/solvent blend was estimated using the UNIFAC method and the Shell Solvent Blend Evaporation Program (AQUEVAP). The evaporation behavior from a free surface of a WBC was experimentally determined and the residual solvent concentration in the wet films was determined and compared with the estimated results. The estimations were in good agreement with the experimental results.

Judging from the residual water/solvent concentration in the wet films during the drying process, WBCs were formulated to
correspond to the composition of the wet films. The rheology and surface tension of these WBCs were determined experimentally. From these data, it became possible to determine the distribution of the viscosity and the surface tension in the wet films, which varies with the initial film thicknesses and produces viscosity and surface tension gradients.

The viscosity of a WBC increases on drying, which decelerates leveling. By contrast, as discussed by Overdiep\cite{19} and Zabel et al.\cite{27}, the surface tension gradient developed in the wet films during drying may accelerate leveling depending on the direction of the gradient. The addition of many solvents to a WBC is known to reduce the surface tension. In other words, the evaporation of the solvent from the wet films of WBCs increases the surface tension and the evaporation of water works to reduce the surface tension. At the initial stage of drying, the evaporation from a unit area of wet films does not depend on the film thickness. This produces variations in the solvent concentration in the wet films depending on the film thickness and results in the development of surface tension gradient.

It is important to control the direction of the surface tension gradient. The direction of the surface tension gradient appears to be strongly affected by the co-solvent added. A solvent which evaporates with the water produces a surface tension gradient that accelerates leveling; high at the trough portion and low at the crest portion of the ripples. When a solvent with lower volatility is employed, the evaporation of the water results in an increase of solvent concentration, which
produces surface tension gradients that make the ripples severe; high at the crest portion and low at the trough portion. Thus, it is important to select the proper co-solvent to obtain a flat smooth coating with a WBC.

**Nomenclature**

- **WBC**: Waterborne coating
- **α(t)**: Total evaporation at time t
- **t**: Decay time after application of coating
- **E(t)**: Evaporation up to time t
- **E₀**: Initial amount of volatile components
- **ν₀**: Initial evaporation rate from WBCs
- **<h₀>**: Initial film thickness
- **n₀**: Initial non-volatile of WBCs
- **NV**: Non-volatile
- **RH**: Relative humidity
- **W₁, W₂**: Weight of aluminum laboratory dish with or without sample
- **i-BuOH**: iso-Butanol
- **WBC/i-BuOH**: Waterborne coating containing 5% i-BuOH
- **TFS**: Tin free steel
- **S**: Shear stress
- **D**: Shear rate
- **N**: The power constant
- **K**: A constant which corresponds to the viscosity at 1 s⁻¹
Relative intensity of the calculated initial evaporation rate based on one at 25°C, 50%RH.

Waterborne coating with no co-solvent

Ethylene glycol mono-hexyl ether

Waterborne coating containing 5% EGHE

Constants of empirical equations

Surface tension

References


CHAPTER 7. LEVELING UNDER A CONTROLLED CONDITION

7-1. Introduction

A new observation method of leveling process has been established as shown in Chapter 5\(^1\) and the occurrence of negative amplitude of surface ripples, as observed by Overdiep\(^2\), was demonstrated for a thermosetting WBC. The leveling speed was also found to greatly depend on the co-solvent added. However, it was difficult to specify the driving force and to understand the mechanism of leveling because of the complex behavior of drying during leveling, which causes changes in viscosity and surface tension, and their distributions on the coated plane depending on the film thickness, as shown in Chapter 6\(^3\). The numerical analysis seems most powerful to dissolve and understand the complex phenomenon. However, it is necessary, to know accurately the proceedings of the drying process and also the leveling process for the analysis. Thus, the leveling experiments were carried out under a controlled condition and the extent of the viscosity gradient and the surface tension gradient were estimated. The effects of the film thickness will be discussed in the following Chapter\(^4\). These results will be used as the basis to discuss the mechanism of leveling.

7-2. Observation of Leveling Process

The leveling experiments were carried out under controlled conditions of 25°C, 65% relative humidity, RH, and negligible air flow. The WBC were applied with a doctor blade having the
knife edge cut to a block shape. The average initial film thickness, $<h_0>$, was 0.12 mm, and the initial amplitude of the surface ripples was set to be 0.05 mm, i.e., $2a_0 = 0.10$ mm. Details of the observation method have been discussed in Chapter 5. 

Fig. 7-1 Observation results of leveling process for WBC/H$_2$O (△), WBC/i-BuOH (○) and WBC/EGHE (●).

Figure 7-1 summarizes the results of observation for the WBC with no co-solvents, WBC/H$_2$O, the WBC containing 5% iso-butanol, WBC/i-BuOH, and the WBC containing 5% ethylene glycol mono-hexyl ether, WBC/EGHE. For the WBC/H$_2$O and WBC/EGHE, the initial portion of the data showed peculiar behavior, i.e., the amplitude of the ripples did not decrease immediately from the initial
amplitude of 0.05 mm. This peculiar behavior is assumed to come from the assumption applied for the observation. As noted previously\textsuperscript{[1]}, the observation system was designed to measure the amplitude of sinusoidally rippled surface, which was applied as a block-shaped surface at the initial stage. It is assumed that the initial stage continued for about 5 seconds because of the slow leveling caused by the combined effects of the nature of the material and the wet film thickness. However, the results were almost consistent with the previous ones\textsuperscript{[1]}, the leveling rate of WBC/i-BuOH is the highest amongst the three WBCs and the WBC/EGHE is the lowest. The negative amplitude or the re-appearance of the surface ripples was observed only in the WBC/i-BuOH, which was consistent with the previous results\textsuperscript{[1]}. It should be noted that the change from crest to trough, and vice versa, occurred twice, and finally the magnitude of the ripples gave a positive value in the observation of the WBC/i-BuOH.

It would be reasonable to assume that the negative amplitude of the surface ripples, or the change from crest to trough, occurs as a result of leveling flow, i.e., by some force to reproduce surface ripples contained in the fluid motion or produced by the results of leveling flow. At first, it seemed as if the force of inertia was responsible for the phenomenon, although it had been thought to be negligible\textsuperscript{[1,5-15]}. The magnitude of inertia is related to the velocity of the moving mass, and if the leveling flow is reasonably slow the effects will be negligible, as in the cases considered previously\textsuperscript{[2,4,4,9]}. However, it is doubtful if it is reasonable to neglect the
effects in the present case, when leveling proceeds very quickly. Moreover, the fact that the negative amplitude of the surface ripples is observed only for the WBC with the highest leveling rate, and vice versa, strongly suggests that the contribution of the force of inertia might not be negligible.

The other possible factors which could produce the negative amplitude of the surface ripples is the surface tension gradient, the distribution of surface tension, produced because of the variation of the film thickness during drying and leveling flow. During the drying process, a surface tension gradient is produced, as pointed out by Overdiep[1] and others[1,16]. In the case of the WBC/i-BuOH, the surface tension at the trough portion of the surface ribs tends to be higher than that at the crest portion. By leveling flow the material in the crest portion, with lower surface tension, flows into the trough portion and mixes with the material there with a higher surface tension. This tends to reduce the surface tension of the material in the trough portion, however, the surface tension of the material in the trough portion continues to be higher, until a negative amplitude of the ripples occurs. This surface tension gradient might work to produce a crest at the portion where the trough initially was, by the well defined "surface tension driven flow"[17,12].

7-3. The Viscosity Gradient in the Coated Wet Film

The viscosities of the WBCs are given in Chapter 6 as a function of the total evaporation[3]. The composition of residual volatile components in the wet films of WBCs containing
a variety of co-solvents is also given there as a function of the average initial film thickness and the time after application. The viscosity gradients were calculated using these data neglecting the effects of leveling flow. For the calculation of the viscosity at a given value of the total evaporation, linear interpolation was applied.

Combining Eqs. 5-1, 5-2, 5-3 and 5-5, the viscosity $K(t)$ can be expressed as a function of $t$ and $\langle h_0 \rangle$, which produces the viscosity distribution in the wet film depending on the variation in film thickness during the drying process. Neglecting the effects of leveling flow, the distribution of $K(t)$ is illustrated in Fig. 7-2 for WBC/H$_2$O when the observations of the leveling process were carried out, at 25°C, 65% RH.

![Viscosity gradient during drying at 25°C, 65%RH for WBC/H$_2$O](image)

**Fig. 7-2** Viscosity gradient during drying at 25°C, 65%RH for WBC/H$_2$O
The distribution of $K(t)$ for WBC/i-BuOH and WBC/EGHE showed a pattern similar to that of WBC/H$_2$O. The viscosity of the crest portion of ripples is lower than that of the trough portion. This means that it is easier to flow from the crest to the trough as compared to the opposite direction. However, the viscosity distribution itself is not thought to work as a driving force in promoting leveling. Moreover, it is obvious that the viscosity build-up reduces the leveling flow rate.

7-4. The Surface Tension Gradient in the Coated Wet Film

The surface tension gradient in the wet film can be estimated by the same manner as the calculation of the viscosity gradient shown above.

![Surface tension gradient](image)

*Fig. 7-3* Surface tension gradient during drying at 25°C, 65%RH for WBC/H$_2$O
Fig. 7-4 Surface tension gradient during drying at 25°C, 65%RH for WBC/i-BuOH

Fig. 7-5 Surface tension gradient during drying at 25°C, 65%RH for WBC/EGHE
Figures 7-3, 7-4 and 7-5 show the estimated results of the surface tension gradient for WBC/H₂O, WBC/i-BuOH and WBC/EGHE, respectively. The distribution patterns of WBC/H₂O and WBC/EGHE are similar, although the absolute level of the surface tension is different. However, the distribution pattern of WBC/i-BuOH is quite different from that of the others, as suggested by the change in the surface tension during the drying process[^1].

It is well known that liquids tend to contract to form spheres at the boundary by the force of surface tension. A coated liquid film is thought to be balanced and to produce a flat film when no surface tension gradient exists in the film. However, materials with a lower surface tension will be pulled by the materials with a higher surface tension when a surface tension gradient exists in the film, which is the so-called "surface tension driven flow". When the surface tension of the material at the trough portion is higher than that at the crest portion, the materials at the crest portion will be pulled to the trough portion, which accelerates leveling flow, as in the case of WBC/i-BuOH. Contrarily, as in the cases of WBC/H₂O and WBC/EGHE, when the surface tension of the material in the crest portion is higher than that in the trough portion, the material is pulled towards the crest, which decelerates leveling or makes the ripples even more severer. The observed results are consistent with this estimation.

[^1]: Reference or citation
7-5. Estimation of the Driving Force to Promote Leveling

As noted, Orchard et.al. thought that the driving force to promote leveling was the hydrostatic pressure gradient in the film caused by surface tension and the free boundary curvature of the film\(^{[5,1]}\). Their theory was experimentally verified for fluids with no volatile components, but it failed to even qualitatively describe the leveling process of fluids containing volatile components \(^{[1,2]}\). This means that one of the primary forces promoting leveling is introduced due to the hydrostatic pressure gradient and the other primary force is due to the rheological changes caused by the evaporation of volatile components, which will accelerate or decelerate leveling.

As noted above, the surface tension gradient produced by the evaporation of the volatile components could be one of the primary forces promoting leveling. Assume that the coated film is divided into segments, for example crest segments and trough segments. In the case of WBC/i-BuOH, the surface tension of the trough segments increases to 45 mN/m during the drying process, whereas that of the crest segments increases only to 39 mN/m, see Fig. 7-4. The difference, $\Delta \gamma = 6$ mN/m, is thought to work as a force promoting leveling. Assuming that the tension is homogeneously distributed throughout the interface of the segments, the stress working at the interface due to the surface tension difference, $\tau _{\Delta \gamma}$, is evaluated as follows;

$$\tau _{\Delta \gamma} = \Delta \gamma / \langle h_0 \rangle$$  

(7-1)

Orchard\(^{[5]}\) analyzed the stress in the coated film due to the hydrostatic pressure gradient caused by surface tension and
the free boundary curvature of the film, and derived the maximum shearing stresses for some limiting cases as follows:

\[ \tau_1 = \gamma ak^3 h \]  
\[ \tau_2 = \gamma ak^4 h^2 \]  
\[ \tau_3 = \gamma ak^2 / e \]

(7-2)  
(7-3)  
(7-4)

where, \( a \) is the amplitude of the surface ripples, \( k = 2\pi / \lambda \), \( h \) is the depth of the coated film beneath the surface irregularity, \( e \) is the natural base, \( \pi \) is the ratio of circumference, and \( \lambda \) is the wave length of the surface ripples. These maximum shearing stresses can be calculated using the experimental variables. Table 7-1 shows the calculated results using the variables from the leveling experiments and compared with the calculated result of \( \tau_{\Delta \gamma} \). In these calculations, \( \langle h_0 \rangle \) was used in the place of \( h \), which will result in somewhat larger values for the maximum shearing stresses. It is surprising that the magnitude of the stress due to the surface tension gradient is much greater than that due to the hydrostatic pressure gradient, although the surface tension difference was thought not to be so large because of the mixing of the materials due to the leveling flow. It is still worth noting that the stress due to the surface tension difference played a prominent role in promoting leveling in the present experiments.

In practical cases when the surface ripples possess a sinusoidal profile, it is much more complicated to estimate the development of the surface tension gradients and the stresses due to them. The results of the analysis by the numerical
Table 7-1  Estimated results of $\tau_{\Delta Y}$, $\tau_1$, $\tau_2$ and $\tau_3$

<table>
<thead>
<tr>
<th>Stresses</th>
<th>Estimated Values $(N/m^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{\Delta Y}$</td>
<td>40</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>1.07</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>0.25</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>1.68</td>
</tr>
</tbody>
</table>

technique for such cases will be dealt in the following chapters.

It is presumed that the entropy of mixing could produce some forces to accelerate or decelerate leveling flow, because materials with a different composition are mixed by the leveling flow process. However, it is difficult to consider the effects of mixing to understand the mechanism of leveling and it is not considered here.

7-6. Concluding Remarks

Leveling experiments were carried out under controlled conditions to understand the mechanism of leveling of coated thermosetting WBC films. Consistent results were obtained with the previous observations.

The developments of surface tension gradients and viscosity variations under the conditions were estimated using the results of the evaporation behavior shown in Chapter 6. Comparison of the estimated stress due to the surface tension gradients with the maximum shearing stresses due to the hydrostatic pressure gradients derived by Orchard, revealed that the stress due to the surface tension gradients could be much greater than the latter.
and that it is meaningless to discuss the leveling behavior without any account for its contribution.

**Nomenclature**

- \( <h_0> \) : Initial film thickness in average
- \( RH \) : Relative humidity
- \( a_0 \) : Initial amplitude of surface ripples
- \( WBC/H_2O \) : WBC with no co-solvent
- \( WBC/i-BuOH \) : WBC containing 5% iso-butanol
- \( WBC/EGHE \) : WBC containing 5% ethylene glycol mono-hexyl ether
- \( K(t) \) : Viscosity of coated films at 1 \( s^{-1} \)
- \( t \) : Decay time after application of WBC
- \( \gamma(t) \) : Surface tension of the coated wet film
- \( \Delta\gamma \) : Surface tension difference during drying
- \( \tau_{\Delta\gamma} \) : Stress to promote leveling flow due to the surface tension difference
- \( \tau_1, \tau_2, \tau_3 \) : Maximum shearing stresses derived by Orchard
- \( a \) : Amplitude of surface ripples
- \( k = 2\pi/\lambda \)
- \( h \) : Depth of the film beneath the surface irregularity
- \( e \) : The natural base
- \( \pi \) : The ratio of circumference
References


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CHAPTER 8. EFFECTS OF FILM THICKNESS ON THE LEVELING PROCESS

8-1. Introduction

During the leveling experiments, the observation became difficult due to cratering and the fast leveling rate for the thick films. In other words, the leveling rate of the thermosetting WBC was strongly dependent on the initial film thickness. Thus, the effects of the average initial film thickness on the leveling rate was studied here using a thermosetting WBC.

Concerning the relationship between the leveling rate and the average initial film thickness, Orchard\(^1\) and then Patton\(^2\) showed that the leveling rate is proportional to \(1/\langle h_0 \rangle^3\), where \(\langle h_0 \rangle\) is the average initial thickness of the coating film. The assumption of homogeneous and constant surface tension and viscosity, i.e., the coating material without any volatile components, was employed in their treatments. However, as noted above, such treatments fail to describe the leveling behavior of coating films with some volatile components. Thus, it is worth experimentally determining the effects of average film thickness on the leveling rate to understand the leveling mechanism of thermosetting WBC.

8-2. Rheological Properties during Drying

A waterborne epoxy/phenolic/acrylic coating, WBC/EGHE, was used here which contains 5% ethylene glycol mono-hexyl ether, EGHE. As shown in Chapter 5, five WBC were prepared, which correspond to the total evaporation of 0, 0.030, 0.060, 0.090 and
The following assumptions were made to prepare the WBC; (1) EGHE does not evaporate from the coated film, (2) only water evaporates from the coated film at the rate shown in Table 6-2. Table 8-1 summarizes the characterization results of the viscosity and the surface tension during drying.

Table 8-1 The viscosities and surface tensions of WBC during drying.

<table>
<thead>
<tr>
<th>Total Evaporation</th>
<th>Viscosity at 1 s⁻¹ (Pa·s)</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.602</td>
<td>33.5</td>
</tr>
<tr>
<td>0.03</td>
<td>0.938</td>
<td>33.0</td>
</tr>
<tr>
<td>0.06</td>
<td>1.274</td>
<td>32.6</td>
</tr>
<tr>
<td>0.09</td>
<td>1.610</td>
<td>32.1</td>
</tr>
<tr>
<td>0.12</td>
<td>1.946</td>
<td>31.7</td>
</tr>
</tbody>
</table>

8-3. Observation of Leveling Process

The leveling experiments were carried out under a controlled condition of 25°C, 65% relative humidity, RH, and negligible air flow. The WBC was applied by means of a doctor blade with the knife edge cut to a block shape. Details on the observation method have been shown in Chapter 5. The initial amplitude of the surface ripples was set to be 0.05 mm, i.e., 2a₀ = 0.10 mm.

Figure 8-1 shows the observation results of the leveling process. It is clear that the thicker the film is, the faster the leveling proceeds. This seems consistent to the prediction of Orchard¹ and Patton².

However, this seems peculiar because the thicker the film is, the less the surface tension gradient, i.e., one of the
Fig. 8-1 Observation results of leveling process of a thermosetting waterborne coating with various wet film thickness, \( h_0 \). Marks denote: \( \triangle: 0.12 \text{ mm} \), \( \Delta: 0.15 \text{ mm} \), \( \bullet: 0.20 \text{ mm} \) and \( \circ: 0.25 \text{ mm} \).

Fig. 8-2 Viscosity gradient of WBC/EGHE during leveling at 25°C, 50% RH.
driving forces to promote leveling is, see Fig. 7-5, where the
distribution of the surface tension is plotted. The Figure
also shows that the surface tension of the coated film decreases
during the drying process, which will work to decelerate
leveling. The viscosity gradient shown in Fig. 8-2 is not
very steep, and may not decelerate the leveling so much.
These findings show that it is impossible to explain the
phenomenon by only the effects of surface tension gradient.

![Graph showing relationship between log(a/a₀) and time](image)

*Fig. 8-3 Replot of Fig. 8-1 using the same marks.*

Initial portions of the data in Fig. 8-1 were replotted in
Fig. 8-3 to show the relationship of \( \log(|a/a₀|) \) vs. time, and the
time to achieve \( \log(|a/a₀|) = -2.0 \), \( t_{1/100} \), was determined by linear
extrapolation. Using the results, \( 1/t_{1/100} \) was determined as
a measure of the leveling rate. If the theory of Patton\textsuperscript{[2]} is valid, then the leveling rate is reversely proportional to $\langle h_0 \rangle^{-3}$. Figure 8-4 shows the results with the predicted results obtained by the modified Patton's theory discussed below, where the effects of viscosity build-up and surface tension decrease are accounted for. The Figure shows that the observed leveling rate is much faster than that predicted by Patton's theory. The observed $t_{1/100}^{-1}$ appears to be a linear function of $\langle h_0 \rangle^{-3}$, whereas the calculated $t_{1/100}^{-1}$ does not, which contradicts to the prediction. The calculated results without account for the effects of drying, i.e., the change of surface tension and viscosity during leveling, showed little

![Figure 8-4](image)

Fig. 8-4 Leveling rate $t_{1/100}^{-1}$ vs. $\langle h_0 \rangle^{-3}$. \(\circ\) denotes observed data, and \(\Delta\) denotes the predicted data by Patton's theory.
difference with the calculated results shown above.

Thus, both theories, one based on the surface tension gradient and one based on the hydrostatic pressure gradient caused by surface tension and the free boundary curvature of the film, fail to describe the leveling process. However, the faster leveling rate of observation than the prediction suggests that there may be another component of force to promote leveling. Another component is assumed to be the surface tension gradient.

However, the observed data shown in Fig. 8-4 suggests that it takes about 3 s to achieve $\log(|a/a_0|) = -2.0$, $t_{1/100}$ for infinite $<h_0>$ for the coating material and the shape of the surface ripples employed here, because $t_{1/100}^{-1}$ approaches 0.3 when $<h_0>^{-3}$ approaches zero. Thus, it seems possible to predict the ultimate leveling rate by this procedure for thicker films.

8-4. Revision of Patton's Theory

Patton[1] considered a wavy surface corresponding to the set of conditions diagrammed in Fig. 8-5 to calculate the liquid pressure that the surface tension exerts during the leveling process. He considered the force acting on the crest of the ridge of wet paint having length $L$, which can be unity, and a radius of curvature $r$ (the bottom of the crest segment is bounded by the chord $C=a/2$, which subtends arc $a_c$ of the ridge).

The precise revision of his theory shows that he considered only the force caused by the crest segments forgetting the force acting in the opposite direction with the same magnitude due to
the trough segments. Both forces are thought to act to accelerate leveling and so the right side of Equation 11 on page 117 of his book should be doubled, which is balanced with the viscous resistance. Thus, the volumetric flow rate should read as follows, replacing nomenclature and setting $L$ to be unity:

$$\frac{dV}{dt} = -\frac{4}{3} \frac{<h_0>^3 \cdot \gamma(t)}{r \cdot \lambda \cdot \eta(t)}$$

(8-1)

where $\eta(t)$ is the viscosity of the coated fluid at time $t$ after application, which could be replaced by $K(t)$ in Eq. 6-5.

Fig. 8-5 Schematic illustration of striated wet film undergoing leveling.

Because the distribution of viscosity and surface tension is not considered, it is reasonable to assume that the total evaporation, $a(t)$ is also homogeneous independent of the film
Thus, $a(t)$ is given simply as follows:

$$a(t) = \frac{v_0}{(1-n_0)\cdot<h_0> \cdot t} \quad (8-2)$$

Replaced as:

$$A' = A\times \frac{v_0}{(1-n_0)\cdot<h_0>}, \quad C' = C\times \frac{v_0}{(1-n_0)\cdot<h_0>}$$

Eq. 8-1 is reduced as follows:

$$\frac{dV}{dt} = -\frac{4}{3} \cdot \frac{<h_0>^3}{r \cdot \lambda} \cdot \frac{C' \cdot t + D}{A' \cdot t + B} \quad (8-3)$$

On the other hand, the volume of the crest is given by Patton as follows:

$$V_c = \frac{(\lambda/2)^3}{12r} \quad (8-4)$$

and the relationship between the radius of surface curvature, $r$, and the amplitude of surface ripples, $a$, is given as follows:

$$r = \frac{0.031\lambda^3}{a} \quad (8-5)$$

8-5. Numerical Analysis

The equations in the prior section make it possible to calculate the course of the amplitude change, i.e., the leveling process, by a stepwise numerical method. Note that only the effects of hydrostatic pressure gradient caused by the surface tension and the free boundary curvature were considered in this case, forgetting the effects of surface tension gradient, although the changes in the viscosity and the surface tension by the evaporation of volatile components during the leveling
process was well accounted for.

In these equations, \( V_0, n_0, A, B, C \) and \( D \) are the constants characteristic to the specific WBC and to the atmospheric conditions. \( a_0, \langle h_0 \rangle \) and \( \lambda \) are the constants determined by the experimental conditions. Table 8-2 shows some of these constants. \( A' \) and \( C' \) are shown in Table 8-3 as a function of \( \langle h_0 \rangle \). Note that the density of the fluid assumes unity here, which would not have a great influence on the calculation results.

Numerical analysis was carried out as follows. First, the radius \( r_0 \) at \( a = a_0 \), i.e., at \( t = 0 \), was calculated using Eq. 8-5. By substituting the value into Eq. 8-4, the initial volume of crest, \( V_{c,0} \), is known. Substitution of \( r_0 \) and \( t = 0 \) into Eq. 8-3 gives the rate of volumetric change at \( t = 0 \). Thus, the volume of the crest at \( t = \Delta t \), \( V_{c,\Delta t} \), is calculated as follows:

\[
V_{c,\Delta t} = V_{c,0} + \frac{dv}{dt} \Delta t
\]  

Substitution of this result into Eq. 8-6 gives the radius of curvature at \( t = \Delta t \), \( r_{\Delta t} \). Substitution of \( r_{\Delta t} \) into Eq. 8-5 gives the amplitude of surface ripples at \( t = \Delta t \), \( a_{\Delta t} \). By repeating this procedure, the amplitude change of the surface ripples is obtained.

Fig. 8-6 shows the results of calculation, where the results of calculation when no changes in viscosity nor surface tension during leveling were assumed, i.e., \( \alpha(t) = 0 \), are also shown. Comparison of the results with Fig. 8-1, where experimentally
Table 8-2 Coefficients in the empirical equations, Eq. 6-5 and 6-6.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Estimated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>11.2 Pa·s</td>
</tr>
<tr>
<td>$B$</td>
<td>0.602 Pa·s</td>
</tr>
<tr>
<td>$C$</td>
<td>-15.3 mN·m$^{-1}$</td>
</tr>
<tr>
<td>$D$</td>
<td>33.5 mN·m$^{-1}$</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>3.33×10$^{-5}$ mN·mm$^{-2}$·s$^{-1}$</td>
</tr>
<tr>
<td>$n_0$</td>
<td>0.30</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>4.0 mm</td>
</tr>
<tr>
<td>$a_0$</td>
<td>0.05 mm</td>
</tr>
</tbody>
</table>

Fig. 8-6 Predicted leveling process by the modified theory assuming $\alpha(t) = \frac{\nu_0}{(1-n_0)\cdot\langle h_0 \rangle} \cdot t$ and $\alpha(t) = 0$. Marks denote: ▲: 0.12 mm, △: 0.15 mm, ●: 0.20 mm and ○: 0.25 mm.
determined leveling processes are shown, revealed that the predicted process of leveling by Patton's theory proceeds much more slowly than the observed ones as shown in Fig. 8-4, and drying had little effect on the process, although the leveling rate of the process without taking into account the effects of viscosity and surface tension change is slightly higher.

It is obvious from Eq. 8-1 that the increase in viscosity due to evaporation of volatile components works to reduce the volumetric flow rate as well as the decrease in surface tension. In other words, both the increase in viscosity and the decrease in surface tension decelerate leveling.

Thus, the results shown in Fig. 8-4 and 8-6 are as expected. However, the calculated leveling rates are much lower than those observed, although the volumetric flow rate is doubled here from the original theory[2]. This discrepancy is thought to come from the assumption of the original theory that the leveling flow is driven only by the hydrostatic pressure gradient caused by surface tension and the free boundary curvature. This emphasizes the importance to account for the contribution of surface tension gradient together with the hydrostatic pressure

<table>
<thead>
<tr>
<th>$&lt;h_0&gt;$</th>
<th>$\lambda'$</th>
<th>$C'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.00444</td>
<td>-0.00607</td>
</tr>
<tr>
<td>0.15</td>
<td>0.00355</td>
<td>-0.00485</td>
</tr>
<tr>
<td>0.20</td>
<td>0.00267</td>
<td>-0.00364</td>
</tr>
<tr>
<td>0.25</td>
<td>0.00213</td>
<td>-0.00291</td>
</tr>
</tbody>
</table>
gradient to discuss the mechanism of leveling flow.

8-6. Concluding Remarks

The leveling of a thermosetting waterborne coating with various average film thicknesses has been considered. Patton's theory predicts that the leveling rate is reversely proportional to \( h_0^3 \). A linear relationship was obtained for the observed leveling rate against \( h_0^{-3} \). However, the leveling rate was much higher than that predicted. This discrepancy is thought to come from the assumption made in the original theory; (1) the leveling flow is induced only by the hydrostatic pressure gradient caused by surface tension and curvature of the free boundary surface, and (2) the surface tension and the viscosity of the fluid is constant during the leveling process and homogeneous throughout the film independent of the film thickness. However, the linearity of the leveling rate \( t_{1/100}^{-1} \) vs. \( h_0^{-3} \) plot suggests that the hydrostatic pressure gradient in the coated film plays an important role as a component of driving force to promote leveling flow.

The original theory of Patton was revised here as to give proper force balance and modified to include the changes in surface tension and viscosity during leveling by evaporation of volatile components in the coating material, although the assumption of homogeneity of surface tension and viscosity throughout the film was maintained. The numerical solutions of the modified theory gave a slightly higher leveling rate, but still much lower than the observed ones. This means again
that it is difficult to describe the leveling process with only one driving force, i.e., hydrostatic pressure gradient in the film, even though the changes in surface tension and viscosity during leveling by evaporation of volatile components in the fluid are accounted for. Thus, the importance is emphasized again to consider the surface tension gradient in the film caused by the distribution of film thickness and evaporation of volatile components in the fluid as a component of the driving force to promote leveling.

\textbf{Nomenclature}

\begin{itemize}
  \item \textit{WBC} : Waterborne coating
  \item $<h_0>$ : Average initial film thickness
  \item \textit{EGHE} : Ethylene glycol \textit{mono}-hexyl ether
  \item $K(t)$ : Viscosity at 1 $s^{-1}$
  \item \textit{RH} : Relative humidity
  \item $a_0$ : Initial amplitude of surface ripples
  \item $A, B, C, D$ : Constants in the empirical equations Eqs. 6-5 and 6-6
  \item $a(t)$ : Total evaporation
  \item \textit{WBC/EGHE} : WBC containing 5\% EGHE
  \item $a$ : Amplitude of surface ripples at time $t$
  \item $t_{1/100}$ : Time to achieve $\log(\|a/a_0\|) = -2.0$
  \item $L$ : Length of surface ripples
  \item $r$ : Radius of surface curvature
  \item $C$ : Chord length ($= \lambda/2$)
\end{itemize}
\( \lambda \) : Wave length of surface ripples

\( a_c \) : Arc length of surface ripples

\( \eta(t) \) : Viscosity at time \( t \)

\( \gamma(t) \) : Surface tension at time \( t \)

\( n_0 \) : Initial non-volatiles of the WBC

\( V_0 \) : Initial evaporation rate

\( A' \) : 
\[ A' = A \times \frac{V_0}{(1-n_0)\langle h_0 \rangle} \]

\( C' \) : 
\[ C' = C \times \frac{V_0}{(1-n_0)\langle h_0 \rangle} \]

\( V \) : Volume of fluid

\( V_c \) : Volume of crest

\( r_0 \) : Radius of surface curvature at \( t=0 \)

\( V_{c,0} \) : Volume of crest at \( t=0 \)

\( \Delta t \) : Increment of time

\( V_{c,\Delta t} \) : Volume of crest at \( t=\Delta t \)

\( r_{\Delta t} \) : Radius of surface curvature at \( t=\Delta t \)

\( a_{\Delta t} \) : Amplitude of surface ripples at \( t=\Delta t \)

References


CHAPTER 9. CHEMICAL STRUCTURE OF CURED EPOXY FILMS

9-1. Introduction

The requirement to reduce can manufacturing costs leads to the reduction of the total materials used. This includes the reduction of the thickness of can stock and reduction of the area of the can end, by a severe neck-in of the can body. These fabrication limitations result in the requirement of coating films of high flexibility. Moreover, flexible vinyl coatings are undesirable from an environmental view, especially in Europe and Japan, although these coatings have been feasibly used where high flexibility is required.

Epoxy/phenolic solvent borne coatings\(^{[1-5]}\) and waterborne coatings based on epoxy/phenolic with acrylic components\(^{[6-12]}\) have been widely used for the interior coating of cans. However, their limited flexibility result in their limited use and vinyl coatings have been applied for corrosive packs. Because of the excellent adhesion and corrosion resistance of epoxy/phenolic coatings, improvement of their flexibility is thus highly desired.

The use of epoxy resins of higher molecular weight can be a solution to this requirement. However, because of the higher viscosity of those solutions, more solvents is required to formulate solvent-borne coatings and also in the manufacturing of waterborne coatings, an obvious disadvantage.

Many studies have been carried out to understand the relationship between the structure and the performance of cured epoxy resins\(^{[13-17]}\). The molecular weight of the network chain,
Several procedures have been used to determine $M_c$ based on the theory of rubber elasticity, viz. one using the equilibrium swelling and one using the elastic modulus at the rubbery state in such a temperature region. However, relatively small values of $M_c$ were obtained by these treatments, which themselves violated the applicability of the theory, i.e., the cured epoxy resins were not rubbery enough to apply the theory of rubber elasticity.

Here, we propose a new procedure to determine $M_c$ using the theory of the partitioning of components between sol and gel proposed by Flory. We define the sol to be the components soluble in solvents and the gel to be the network polymer. Then, by modeling the curing reaction, $M_c$ can be calculated using the gel content data in the cured film. Comparison with the results obtained in swelling experiments show that reasonable results are obtained by this procedure in view of film flexibility.

9-2. Theory of Partitioning of Components between Sol and Gel

According to Flory, we consider the probability $\Phi_s$ that a non-crosslinked polymer unit selected at random belongs to the sol fraction in a randomly crosslinked system of any arbitrary primary molecular weight distribution. Then the weight fraction of sol is:

$$w_s = (1 - \rho)\Phi_s + \rho\Phi_s^2 \quad (9-1)$$

where $\rho$ is the degree of crosslinking.

Assuming that each unit may be crosslinked only once, the
probability that a primary molecule composed of \( y \) units possesses \( i \) crosslinked units is:

\[
P_y(i) = \left[ \frac{y!}{(y-i)!i!} \right] \rho^i (1 - \rho)^{y-i}
\]  

(9-2)

The probability that none of the partners of these crosslinked units would belong to an infinite network in the absence of these \( i \) crosslinkages is \( \phi_s^i \). Hence the probability \( s_y \) that a \( y \)-mer primary molecule selected at random is a part of the sol fraction is given by:

\[
s_y = \sum_{i=0}^{y} P_y(i) \phi_s^i
\]  

(9-3)

which reduces to:

\[
s_y = \left( \frac{w_s}{\phi_s} \right)^y
\]  

(9-4)

It follows that:

\[
w_s = \sum_{y=1}^{\infty} w_y s_y = \sum_{y=1}^{\infty} w_y \left( \frac{w_s}{\phi_s} \right)^y
\]  

(9-5)

where \( w_y \) is the weight fraction of primary \( y \)-mer molecules. Thus, if \( w_s \) and \( w_y \) are experimentally determined, then \( \phi_s \) can be calculated. It is obvious from the definitions that:

\[
0 \leq w_s \leq 1
\]  

(9-6)

and:

\[
\sum_{y=1}^{\infty} w_y = 1
\]  

(9-7)

Thus, the value of \( w_s/\phi_s \) is presumed to be slightly smaller than unity. This simplifies the determination of \( \phi_s \) by a stepwise computation.
Once $\Phi_s$ is determined, then the degree of crosslinking $\rho$ can be determined using Eq. 9-1. Furthermore, the crosslink densities in the sol, $\rho'$, and that in the gel, $\rho''$, are given as follows, respectively:

$$\rho' = \rho \frac{\Phi_s^2}{\omega_a}$$  (9-8)

$$\rho'' = \rho \frac{1 - \Phi_s^2}{(1 - \omega_a)}$$  (9-9)

On the other hand, $M_c$ in the gel is given as follows:

$$M_c = \frac{V}{\nu N_0 \rho''}$$  (9-10)

where $V$ denotes the volume of the polymer, $\nu$ denotes the specific volume, and $N_0$ denotes the number of the crosslinkable units in the system.

9-3. Application to Epoxy Coatings

The epoxy resin used was Epikote 1009 supplied by Yuka Shell Epoxy Co., Ltd., Tokyo. Figure 9-1 shows the chemical structure of the resin. Figure 9-2 shows the molecular weight distribution of the epoxy resin determined by gel permeation chromatography, GPC, together with those of sol and gel components for the coating with an epoxy/phenolic ratio of 80/20.

The phenolic resin was derived from $p$-cresol and formaldehyde by condensation reaction using magnesium hydroxide as a catalyst. The resin was purified by a recrystallization technique to contain more than 95% of the substance shown in Fig. 9-1.

In the above discussion, the effects of crosslinker
Fig. 9-1 Chemical structure of the epoxy resin and the phenolic resin.

Fig. 9-2 Molecular weight distribution of the original epoxy resin, the sol component and the gel component in the epoxy/phenolic = 80/20 coating film.
(phenolic resin) has not been taken into account. Such treatment is valid only for systems which include small crosslinkers in size and the crosslinkers do not form any network chain. This condition will be fulfilled for epoxy/phenolic coatings containing the phenolic resin shown in Fig. 9-1. The crosslinking reaction of epoxy/phenolic coatings has been shown to proceed mainly between the methylol group in the phenolic resin and the alcoholic hydroxyl group in the epoxy resin\textsuperscript{[11]}.

To examine the applicability of the above theory, a model calculation was carried out. Figure 9-3 shows the calculated results of $\Phi_s$ using Eq. 9-5 as a function of $\tilde{w}_s$. $\Phi_s$ was found to be slightly larger than $\tilde{w}_s$. Using the values of $\Phi_s$,
obtained above, it is possible to calculate \( \rho \), \( \rho'' \) and \( M_c \) as a function of \( w_s \). Here we used the relationship:

\[
\nu = 1/d
\]  

(9-11)

where \( d \) denotes the density of the material. It is obvious that the quantity \( V \cdot d \) has the dimension of weight. Thus, the quantity \( V/V \cdot N_0 \) is found to denote the reciprocal of the number of components in unit weight of mass. Assuming the chemical structure of the epoxy resin to be expressed as shown in Fig. 9-1, the number of the units in a molecule having a molecular weight of \( M_n \) is:

\[
N_0 = (M_n - 340)/284 + 2
\]  

(9-12)

For a system in which a molecular weight distribution exists, this relation is rewritten:

\[
N_0 = \sum_{y=1}^{\infty} n_0 \cdot w_y = \sum_{y=1}^{\infty} w_y \left[ (M_n - 340)/284 + 2 \right]
\]  

(9-13)

The weight of the system in which \( N_0 \) components are included, \( W \), is expressed as follows:

\[
W = \sum_{y=1}^{\infty} w_y \cdot M_n
\]  

(9-14)

Thus, Eq. 9-10 is rewritten as follows:

\[
M_c = W/N_0 \cdot \rho''
\]  

(9-15)

Figure 9-4 shows the calculated results of \( \rho \) and \( \rho'' \) as a function of \( w_s \) and Fig. 9-5 shows that of \( M_c \).
Fig. 9-4 Calculated results of $\rho$ (●) and $\rho''$ (○)

Fig. 9-5 Calculated results of $M_c$
9-4. Application to Epoxy/Phenolic Coatings

Epoxy/phenolic coatings were prepared by dissolving the predetermined amount of the epoxy resin, Epikote 1009, and phenolic resin shown in Fig. 9-1 in the mixed solvent of ethylene glycol mono-butyl ether/cyclo-hexanon = 1/1. The resin concentration of the coatings were controlled at 30%.

Figure 9-6 shows the molecular weight distribution pattern for sol extracted by methyl ethyl ketone in baked films with various epoxy/phenolic ratio. The amount of sol in the baked films with a smaller amount of crosslinker tends to be greater and a larger amount of higher molecular weight components of epoxy resin exist in such a sol. In other words, during the process of crosslinking, the higher molecular weight components appear to form a network structure preferentially. As Fig. 9-6 shows, the sol contains some phenolic components. These phenolic components must be excluded from the data to evaluate the amount of sol. Furthermore, \( W_s \) should be evaluated as a ratio of the amount of epoxy resin in the original films to the amount of extracted epoxy resin. If \( W_s \) is evaluated accurately, then \( M_c \) can be determined easily using the relationship shown in Fig. 9-5. Figure 9-7 shows the results obtained for coating films with various epoxy/phenolic compositions. In the Figure, \( M_c \) determined by swelling experiments\(^{116}\) and \( W_s \) are also shown. Swelling experiments were carried out using tetrahydrofuran as a swelling medium. The \( M_c \) determined by swelling experiments were found to be about one fourth of that determined by the new procedure proposed here.

Assuming that \( M_c = 1,000 \) as determined by equilibrium
Fig. 9-6 Molecular weight distribution of the sol fraction in coatings with various epoxy/phenolic ratios.

Fig. 9-7 $M_c$ determined by partitioning theory here (○), that determined by swelling experiments (●), and the sol fraction in the cured films (△).
swelling or elastic modulus in the rubbery temperature region. Then the number of the units in the network chain is estimated to be 3 and the freely rotationable joints to be about 20. Flory showed that the network chains for rubbery materials were composed of 50 to 100 units and contained at least 100 freely rotationable joints. Accordingly, the network structure assumed here is presumed to be rigid and brittle, which is in contradiction to the relatively flexible nature of these coating films. This discrepancy appears to be caused by the application of the theory of the rubber elasticity for the non-rubbery materials, viz. the cured epoxy systems. Thus, the actual values of $M_c$ are presumed to be much greater than the results determined by swelling. This supports the adequateness of results obtained by the new procedure.

9-5. Mechanism of Crosslinking

Figure 9-2 shows the molecular weight distributions of the sol and gel components together with that of the original epoxy resin. The molecular weight distribution of the gel component was determined as the difference of the original sample and the sol component.

Using the data in Fig. 9-2, it is possible to evaluate the progress of the crosslinking reaction. Because the $W_\Phi$ values are known for each fraction, $\Phi_\Phi$, $\rho$ and $\rho''$ can be calculated. Figure 9-8 shows the results for the epoxy/phenolic=80/20 film. In this Figure, the number of crosslinkages in a molecule, $\gamma$, is also shown as a function of molecular weight, which is defined as follows:
Figure 9-8 shows that $\Phi_s$ decreases rapidly with increasing molecular weight. In other words, the higher the molecular weight of the components, the higher is the probability that the molecule is included in the gel. The degree of crosslinking in average, $\rho$, and that in gel, $\rho''$, decreases with the molecular weight, whereas the number of crosslinkages in a molecule, $\gamma$, increases. However, the increase in $\gamma$ is moderate and it increases from 2 at $M_n = 10,000$ to 4 at $M_n = 100,000$. This suggests that the network structure with a higher $M_c$ will be formed by using a higher molecular weight. This finding is supported by the fact that the flexibility of an
epoxy coating film is improved by the use of an epoxy resin with a higher molecular weight.

The concentration of the functional groups in the coating is calculated to be 0.139 equivalents/100g for methylol group and 0.256 equivalents/100g for alcoholic hydroxyl group. Assuming that all methylol groups are consumed in crosslinks and that two network chains are newly formed by the reaction of two methylol groups, the crosslinks introduced in an epoxy molecule is estimated to be ca. 4.5 and the molecular weight of the network chain, \( M_c = 500 \). However, these assumptions result in the underestimation of \( M_c \) because the methylol groups are consumed by their condensation reaction and the sol component contains some phenolic components, see Fig. 9-5. Thus, the magnitude of \( M_c \) must be much greater than that estimated here. This also supports the \( M_c \) evaluated using the partitioning theory of components between sol and gel.

9-6. Concluding Remarks

The theory of the partitioning of components between sol and gel proposed by Flory was employed to estimate the network structure of cured epoxy/phenolic coatings. The magnitude of the molecular weight of the network chain was evaluated and compared with the results determined by swelling. The following conclusions were derived:

(1) The network structure of cured epoxy films can be estimated using the molecular weight distribution of the starting epoxy resin and that of the sol component. The molecular weights of the network chain were estimated to be 2,000 to 3,000 for the
coating films with 10 to 15 percent sol fraction. These values are much greater than those evaluated using swelling data, but appeared much reliable than the later.

(2) The crosslinking was found to proceed by the inclusion of larger molecules into the network preferentially. In the cured films, the sol components were composed of lower molecular weight components of epoxy resin and part of the crosslinker.

(3) The higher the molecular weight of the original epoxy resin, the higher the molecular weight of the network chains in the cured film tends to be. This suggests that more flexible films can be obtained using epoxy resins with a higher molecular weight.

Nomenclature

\[ M_c \] : Molecular weight of network chains
\[ \Phi_s \] : The probability that a non-crosslinked polymer unit selected at random belongs to the sol fraction
\[ w_s \] : The weight fraction of sol
\[ \rho \] : The degree of crosslinking
\[ y \] : The number of components in a molecule
\[ i \] : The number of crosslinked units in a molecule
\[ s_y \] : The probability that a y-mer primary molecule selected at random is a part of the sol fraction
\[ w_y \] : The weight fraction of primary y-mer molecules
\[ \rho' \] : The crosslinking density in the sol
\[ \rho'' \] : The crosslinking density in the gel
\[ V \] : The volume of the polymer
\( v \) : The specific volume
\( N_0 \) : The number of crosslinkable units in the system
\( GPC \) : Gel permeation chromatography
\( d \) : Density of the system
\( n_0 \) : The number of the components in a molecule having molecular weight \( M_n \)
\( M_n \) : Number based molecular weight
\( W \) : The weight of the system in which \( N_0 \) components are included
\( \gamma \) : The number of crosslinkage in a molecule

References

CHAPTER 10. FLEXIBILITY OF EPOXY COATING FILMS

10-1. Introduction

As discussed in the previous chapter, epoxy coatings with improved flexibility are highly desired in the can manufacturing industry. The flexibility of epoxy coating films has been suggested to be improved by selecting an epoxy resin with a smaller content of lower molecular weight components, from the analysis of the chemical structure of cured films[1].

In this chapter, we experimentally obtained epoxy resins with a sharper molecular weight distribution by liquid-liquid extraction and formulated solvent-borne coatings with a phenolic crosslinker. Solvent-borne coatings were also formulated using commercial epoxy resins having various molecular weights and the blended resins of Epikote 1009 and Phenoxy resin PKHH. Using these coatings, the flexibility of the cured films are discussed with regard to the structural parameters.

10-2. Effects of Low Molecular Weight Components

A larger amount of lower molecular weight components is presumed to be included in the sol component than of higher molecular weight components because the number of functional groups in a molecule for the former is less than for the later. In other words, the crosslinking reaction for the epoxy resin which contains more lower molecular weight components proceeds slowly compared with that for epoxy resin with less lower molecular weight components. Furthermore, the lower molecular weight components would tend to form imperfect network struc-
tures, with more chain ends and branches.

To examine the effects of lower molecular weight components, a model calculation was carried out. Assume that the molecular weight distribution obtained by a gel permeation chromatography, GPC, is segmented into fractions and that each fraction in the sol is formed by the fraction of the original epoxy resin corresponding to the same molecular weight. Then, eliminate a certain fraction both from the original epoxy resin and the sol. The calculated molecular weight of the network chains, $M_c$, for such distributions corresponding to a certain sol content, $W_s$, indicates how $M_c$ changes by elimination of a certain molecular weight fraction. Figure 10-1 shows the calculation results for $W_s=0.10$, 0.15 and 0.20. The contribution of the fractions with a molecular weight range between 1,000 and 3,000.

![Logarithm of Molecular Weight](image)

*Fig. 10-1* $M_c$ change of the cured films by elimination of a segment specified by molecular weight
10,000 appears to be most significant. In other words, a network structure of a higher $M_c$ can be obtained by eliminating such fractions. The influence of fractions with a molecular weight less than 1,000 appears not to be significant. However, this is because of their lower contents and the influence of each molecule may be even more significant. Thus, it will be concluded that the epoxy resin without any lower molecular weight components is preferable to obtain a network structure with a higher $M_c$.

**10-3. Preparation of Liquid-Liquid Extracted Resins**

An epoxy resin, Epikote 1009 supplied by Yuka Shell Epoxy Co., Ltd., Tokyo, was used to prepare epoxy resins with a sharper molecular weight distribution. In a flask, 300 grams of solid epoxy resin was charged with 3,000 grams of ethanol and agitated at the boiling temperature for 3 hours. After being allowed to cool, the mixture separated into two phases. The upper phase, which contained lower molecular weight components, was disposed of. One third of the residue was dried and used to as the extracted resin. By repeating this procedure, epoxy resins with a different molecular weight distribution were obtained. *Figure 10-2 shows the molecular weight distribution patterns of these liquid-liquid extracted resins.*

As *Fig. 10-2* shows, a significant amount of lower molecular weight components was disposed of from the original resin by liquid-liquid extraction; about 20% by 4 successive extractions. This will contribute to the improvement of the flavor aspects of the coating by reducing the migration of these materials into
canned foods and beverages.

Fig. 10-2 Molecular weight distribution patterns of liquid-liquid extracted epoxy resins. Marks denote; ○ : E1009, △ : Extracted 2 times, ▲ : Extracted 3 times, and ● : Extracted 4 times

10-4. Evaluation of Flexibility

The coatings were coated on a 0.21-mm-thick tin free steel, TFS, sheet using a #12 coating bar. The coated sheets were baked in a gas forced air oven at 210°C for either 3 or 5 minutes to obtain films with various degrees of cure. The dry film thickness was about 5 μm.

The evaluation procedure of sol contents is shown in the previous chapter. To evaluate the flexibility of the coating films, the coated panels were cut into 3 by 3 cm specimens and prebended to about 60° to be the coated surface outside. Two folds of the TFS were inserted and fixed. Each specimen was then bumped by dropping a steel block of 3.0 kg at a height of
40 cm (2T-bend).

After being bumped, the specimens were evaluated by an enamel-rater to check the defects caused by bending. An enamel-rater was composed of a potentiostat and an electrolysis unit. A sample was connected to be an anode. Between a stainless steel cathode and the anode, a 6.2-volt direct current, VDC, was loaded using an aqueous solution of 1% sodium chloride as an electrolysis medium, see Fig. 10-3. A sponge block with a 20-mm width was used to control the surface area of the specimen to be evaluated. Just after loading of the voltage for 4 seconds, the current between the anode and the cathode was measured, which corresponds to the area of defects caused by bending\(^{[2]}\). Ten specimens of each sample were evaluated. After eliminating the maximum and minimum values, the average

\(D\)
value of the eight specimens was used as an enamel-rater value, ERV. The lower ERV corresponds to a lower metal exposure area, i.e., better flexibility.

10-5. Flexibility of a Liquid-Liquid Extracted Epoxy Resin

Figure 10-4 shows the $M_c$ corresponding to the molecular weight distributions shown in Fig. 10-2 as a function of $W_s$. The $M_c$ for a given value of $W_s$ increased significantly by eliminating the lower molecular weight components. In other words, the network structure with a certain value of $M_c$ can be obtained with a lower $W_s$, which will contribute to improve the flavor aspects.

![Graph showing $M_c$ as a function of $W_s$.](image)

Fig. 10-4 Calculated $M_c$ for liquid-liquid extracted epoxy resins using the same marks as in Fig. 10-2
Solvent-borne coatings were formulated using the 4 times extracted epoxy resin and the original epoxy resin at various epoxy/phenolic ratios. These coatings were coated on TFS and baked in an oven at 210°C for various time to obtain the coating films with various degrees of cure. Figure 10-5 shows the evaluated results of flexibility by an enamel-rater as a function of calculated $M_c$. The ERVs were well expressed as a function of $M_c$, which has a minimum at around $M_c = 4,000$. In the lower $M_c$ region, the network structure appears to be too tight and rigid; whereas in the higher $M_c$ region, it appears to be loose and imperfect. Thus, it appears important to control $M_c$ to obtain optimum flexibility of the cured coating films, but not $W_s$. 

Fig. 10-5 The relationship between T-bend ERV and $M_c$ for E1009 (○) and liquid-liquid extracted epoxy resins (●).
10-6. Flexibility of Commercial Epoxy Resins

The epoxy resins used were supplied by Yuka Shell Epoxy Co. Ltd., with the trade name of Epikote; E1004, E1007, E1009 and E1010. Phenoxy resin, PKHH, supplied by Union Carbide Co., which was a very high molecular weight version of epoxy resins, was also used.

Figure 10-6 shows the molecular weight distribution patterns of these epoxy resins determined by GPC. The molecular weight distribution pattern of PKHH will be shown later. The phenolic crosslinker used is shown in the previous chapter.

Solvent-borne coatings were formulated at various epoxy/phenolic ratios. These coatings were coated and baked under various conditions to obtain coating films with various degrees of cure. ERVs for T-bended specimens were evaluated and shown in Fig. 10-7 as a function of $M_c$. Although the data scatter slightly, ERVs appear to be expressed as a function of $M_c$. The minimum in ERV appears at $M_c = 3,000$ to 4,000. These $M_c$ values are assumed to be the best to achieve the optimum flexibility for those compositions.

10-7. Flexibility of the Epoxy Resin / Phenoxy Resin Blend System

Solvent-borne coatings were formulated using blended epoxy resins, E1009 and Phenoxy resin PKHH. Figure 10-8 shows the molecular weight distribution patterns of the blended resins. Broader distributions were obtained by blending these resins.

Figure 10-9 shows the evaluation results of flexibility as a function of $M_c$. Surprisingly, the ERVs for blended resins were scattered between those for E1009 and for PKHH. The
Fig. 10-6 Molecular weight distribution patterns of commercial epoxy resins

Fig. 10-7 The relationship between T-bend ERV and $M_c$ for commercial epoxy resins
Fig. 10-8 Molecular weight distribution patterns of E1009/PKHH blend systems. Marks denote; ○ : E1009, ● : E1009/PKHH=3/1, ◦ : E1009/PKHH=2/1, □ : E1009/PKHH=1/1, and • : PKHH

Fig. 10-9 The relationship between T-bend ERV and $M_c$ for E1009/PKHH blend systems using the same marks as in Fig. 10-8
reason for this scattering is still not clear. However, the broad distributions of their molecular weight could be a possible reason. The introduction of lower molecular weight components into PKHH may be a reason for the increased ERVs. By contrast, the introduction of PKHH into a commercial epoxy resin E1009 improves its flexibility, as is well known in the coating industries.

The imperfection of the network structure derived from higher molecular weight components is assumed to be low compared with that derived from lower molecular weight components. Thus, higher molecular weight components may form a network structure with higher perfection at a similar $M_c$. In other words, imperfection may be increased by the introduction of lower molecular weight components.

10-8. Concluding Remarks

The flexibility of epoxy/phenolic coatings were studied systematically in relation to the $M_c$ of cured films. The flexibility of the coating films was found to be expressed as a function of $M_c$ relatively well. The optimum flexibility was found to be achieved at a certain $M_c$ range. In this $M_c$ range, the network chains are assumed to possess sufficient mobility and perfection.

The elimination of the lower molecular weight components from a commercial epoxy resin by liquid-liquid extraction did not cause significant effects on the $M_c$ VS. $W_s$ relationship. However, a higher $M_c$ was achieved at a lower $W_s$; which may help reduce the migration of the sol components in the cured films
into the canned contents and to improve the flavor aspects.

The flexibility of the epoxy resin / Phenoxy resin blend systems could not be expressed as a function of $M_c$. The reason was assumed to be originated from the imperfection of the network structure, which was not considered here.

### Nomenclature

- $GPC$ : Gel permeation chromatography
- $M_c$ : Molecular weight of a network chain
- $w_s$ : Sol content in a cured film
- $TFS$ : Tin free steel
- $VDC$ : Volts direct current
- $ERV$ : Enamel-rater value

### References


CHAPTER 11. SUMMARY

The present thesis is subdivided into three parts.

In the first part, waterborne coatings, WBCs, with excellent film performance were developed, as described in Chapters 2, 3 and 4. A new manufacturing process of WBCs was developed applying a phase inversion emulsification method. The factors affecting the process stability and the factors affecting adhesion performance were analyzed. The morphology of the coatings and the cured films were also analyzed.

In the second part, WBCs with improved leveling performance were developed. The observation system for the leveling process was constructed and the proceeding of the process was accurately determined. The drying processes of coated wet films were also determined. Using these data, the leveling behavior was analyzed for WBCs with various compositions. These findings were described in Chapters 5 - 8.

In the last part, the molecular aspects to develop epoxy resins and their cured films with improved processability and flavor were determined. The processability of the cured films and the flavor aspects could be improved at the same time by using the epoxy resins with less lower molecular weight components. These findings were shown in Chapters 9 and 10.

Chapter 1

The general background on the can manufacturing industry and the themes dealt in the present thesis are reviewed, e.g., the manufacturing process of WBCs, the leveling theories of coated
wet films and the molecular aspects of epoxy resin to develop the flexible cured films.

Chapter 2

A new manufacturing process of high performance WBCs for can coating applications was developed. The manufacturing process is unique; blending an epoxy resin solution and an acrylic resin solution with or without phenolic resin and dispersing the mixture in an aqueous medium by the phase inversion method. The epoxy resins are neither chemically modified by grafting nor esterified by acrylic resin, which is thought to develop the excellent performance of epoxy/phenolic coatings. By this new process, a variety of resins can be emulsified with minimum effects of the surfactant acrylic resin. Thus, latitude to design formulations was widened and the performance of epoxy resin and its hardener could be fully developed.

Chapter 3

High performance WBCs were developed which could be utilized as an adhesion primer for sideseam bonded cans. The factors affecting adhesion performance were studied systematically and found that the effects of excess amount of the acrylic surfactant are not significant, but those of the neutralizer amines are significant. Thus, the use of amines with branched alkyl group, cyclic amines or ammonia are shown to be preferable.

Chapter 4

The morphology of the coatings and cured film was charac-
eralized and found to be quite different from the conventional 
WBCs, i.e., the acrylic-modified epoxy resin systems. 
Acrylics and epoxy/phenolic resins exist in separate phases in 
the cured film, and the epoxy/phenolic resin constitutes a 
continuous phase. Such a structure, acrylic resin dispersed 
epoxy/phenolic polymers gives the cured films the inherent 
characteristics of the epoxy/phenolic polymer chemically and 
physically. Thus, the tough and chemically resistant 
characteristics of the epoxy/phenolic polymers are maintained and 
the cured film shows excellent hot water resistance. Although 
the epoxy/phenolic polymers are not in direct contact with the 
substrate and the mechanism of adhesion to the substrate differed 
from the case of solvent-borne coatings, excellent adhesion to 
the substrate was also developed.

Chapter 5

A modified observation system for the leveling process of 
a coated fluid was proposed, and the observation findings were 
presented and compared with previous results. For the 
thermosetting WBCs, the theory of Orchard et al. and those based 
on it were not applicable and failed to give even a qualitative 
description.

The theory of Overdiep was found to be reasonable, but, it 
was insufficient to predict the leveling performances of coating 
materials without experimentation. Qualitatively, the 
original theory suggests the possibility of the re-appearance of 
the surface ripples, in other words, the occurrence of the 
negative amplitude in the surface ripples during the course of
leveling, although little data was presented regarding the phenomenon.

The co-solvent added plays an important role on the leveling rate and also the occurrence and the control of the negative amplitude of the surface ripples. These are considered to relate closely with the volatility of the co-solvent and the composition of the solvent residue in the coated film during the leveling process. Applying these findings, we succeeded in improving the leveling performance of WBCs for roll coating application.

Chapter 6

The evaporation behavior of the water/solvent blends was estimated by using the universal functional activity coefficient (UNIFAC) method and the evaporation rate from a free surface of a WBC, containing a co-solvent were experimentally determined. These findings were used to estimate the evaporation rate from wet films of a WBC containing a variety of co-solvents with a range of initial thickness. Knowing the composition of the WBC during the drying process, the change in the viscosity and the surface tension was determined. The findings strongly support the development of a surface tension gradient in the film. The development of a surface tension gradient is also suggested to accelerate the leveling of the ribs when a proper co-solvent was employed.

Chapter 7

Experiments on coated films of WBCs under controlled
conditions, i.e., 25°C, 65%RH, were carried out to understand the mechanism of leveling. The data shown in a previous chapter inferred that the development of the surface tension gradients plays an important role in promoting leveling. The stress due to surface tension gradients was found to be much greater than the stress introduced by hydrostatic pressure gradients in the film caused by surface tension and the free boundary curvature of the film. This reconfirms that the use of a co-solvent which evaporates faster than water greatly accelerates the leveling of a WBC.

Chapter 8

The influence of film thickness on the leveling of a thermosetting WBC was examined. The theory of Patton has been revised to give the proper force balance and modified to include the changes in surface tension and viscosity during leveling by the evaporation of volatile components. However, the predicted leveling process by a numerical method did not coincide with the observed results. Thus, the driving force in the theory, hydrostatic pressure gradient in the film, was considered to be insufficient to describe the leveling process of the WBC. The hydrostatic pressure gradient can be a component of driving force to promote leveling, but the existence of another component is suggested.

Chapter 9

The chemistry of network formation for an epoxy/phenolic coating determines the structure of the baked film. The
theory of partitioning of components between sol and gel proposed by Flory was applied to determine the crosslink density and the molecular weight of the network chains, $M_c$. This procedure appears useful to eliminate the problems in the determination procedure of $M_c$ by equilibrium swelling. Using these structural parameters, the mechanism of crosslinking reaction was analyzed and the molecular aspects of epoxy resins to obtain better flexibility were suggested.

Chapter 10

The flexibility of epoxy coating films, crosslinked by a phenolic resin, has been evaluated. The network structures of these films were estimated by the method proposed in Chapter 9. The $M_c$ values of the cured films were found to be controlled to achieve optimized flexibility. This was achieved by the use of an epoxy resin with a higher molecular weight or an epoxy resin with a less content of lower molecular weight components and by control of cure. This also improves the flavour aspect of the cured films.
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